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By: CHRISTIAN E. JUNGE

DIRECTOR METEOROLOGISCH-GEOPHYSIKALISCHES INSTITUT  
JOHANNES GUTENBERG-UNIVERSITÄT  
JOH. JOACHIM BECHER-WEG 1A  
MAINZ GERMANY

SRI Project No. PAU-5644

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## ABSTRACT

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Measurements of aerosol concentration and size distribution were made with a light scattering type particle counter and condensation nuclei counters at sea level and 2200 meter altitudes using sites at Cape Blanco, and Crater Lake, Oregon. Goetz aerosol spectrometer was used to determine size distributions for the chloride and sulfate fractions of the total aerosol. The data collected in marine air masses support earlier findings of sea-spray aerosol size distributions and lack of chemical fractionation during bubble burst aerosol formation. The data indicate that significant amounts of sea spray aerosol do not penetrate to low and mid-tropospheric altitudes above 2000 meters. The aerosols typical of this elevation were found to have size distributions (for radii greater than about  $0.1 \mu\text{m}$ ) well approximated by a power law with an exponent of 3 to 4. They were found to have sulfur to chloride ratios of about 8 and considerable concentrations of substances other than sulfur and chloride. High altitude tropospheric air mass aerosols, observed on this program at Crater Lake during periods of subsidence, have lower concentrations than found for lower altitude tropospheric aerosols and their power law representations are characterized by lower exponential values. Aerosols which were identified with tropospheric levels above 2000 m are believed to be aged aerosols from continental sources rather than sea-surface aerosols transported to higher altitudes.

## FOREWORD

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The purpose of this research study was to obtain information on aerosol chemistry and aerosol particle size distributions in clean Pacific tropospheric air masses entering the west coast of the United States. Observations were made at sea level and in Crater Lake National Park, Oregon, at an altitude of 2200 meters.

Dr. Christian E. Junge, Director, Meteorologisch-Geophysikalisches Institut, Johannes Gutenberg-Universität, Mainz, Germany, was the principal investigator. Dr. Junge was a Visiting Senior Scientist at the Institute during the period from September 1 through November 30, 1965, when the field program was planned and carried out. Dr. Junge completed analysis of the data and the preparation of this report after he returned to Germany.

The research program was carried out in the Atmospheric Sciences Department of Stanford Research Institute. The necessary chemical analyses were provided by the Institute's Chemical Analytical Group. The research equipment was provided by the Institute.

The specific research studies covered by this report were supported by the Atmospheric Physics and Chemistry Laboratory, Environmental Sciences Services Administration, under Contract No. Cwb-11151. Other portions of Dr. Junge's stay at the Institute were supported by the U.S. Air Force under Contract No. AF 19(605)-1941 and by Stanford Research Institute.

Previous research at the Institute had resulted in the development of techniques for determining size distributions of sulfate and chloride aerosol particles in urban atmospheres, and these techniques were the basis for the chemical size distribution phase of this program. Prior

to the actual field sampling, these procedures were carefully reviewed, and Dr. Junge made several improvements to adapt the techniques to the very low concentrations which were expected in this study of tropospheric background aerosols.

The research program described in this report owes a great deal to the efforts and cooperation of several individuals and organizations. The analytical chemistry used in these studies was developed by Dr. Dale M. Coulson. He and Mrs. Lydia Peters assisted Dr. Junge in devising the refinements necessary to deal with the minute samples collected at the remote locations. Mrs. Peters performed the chemical analyses necessary for determination of the sulfate and chloride size distributions.

The cooperation of the personnel at Crater Lake National Park, the U.S. Coast Guard Station at Cape Blanco, and Patrick's Point State Park was indispensable to the success of the field program and is greatly appreciated. Dr. Junge was assisted in the field sampling program by Mr. Elmer Robinson during the first sampling period and by Mr. F. L. Ludwig during the second.

The following report has been authored by Dr. Junge. Details of the instrumentation and the chemical analysis techniques used during the program are presented in two appendices which have been prepared by Mr. F. L. Ludwig, Meteorologist, Stanford Research Institute.

Elmer Robinson, Senior Meteorologist  
Stanford Research Institute

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## I INTRODUCTION

There is a definite lack of tropospheric aerosol size distribution data from air masses which have not been significantly influenced by continental aerosol sources, either natural or anthropogenic. This research program was planned to explore the nature of tropospheric background aerosols as they might exist along the west coast of the United States, and more specifically in northern California and southern Oregon. The remoteness of this area from any major city and the prevailing westerly winds from the Pacific Ocean provided an opportunity for sampling the background tropospheric aerosol without the necessity of using aircraft, although it was obviously still necessary to choose sampling sites carefully to avoid local contamination. At coastal locations we attempted to avoid areas where heavy spray would dominate, but we were only partly successful in this goal.

## II SAMPLING LOCATIONS AND FIELD TEST PERIODS

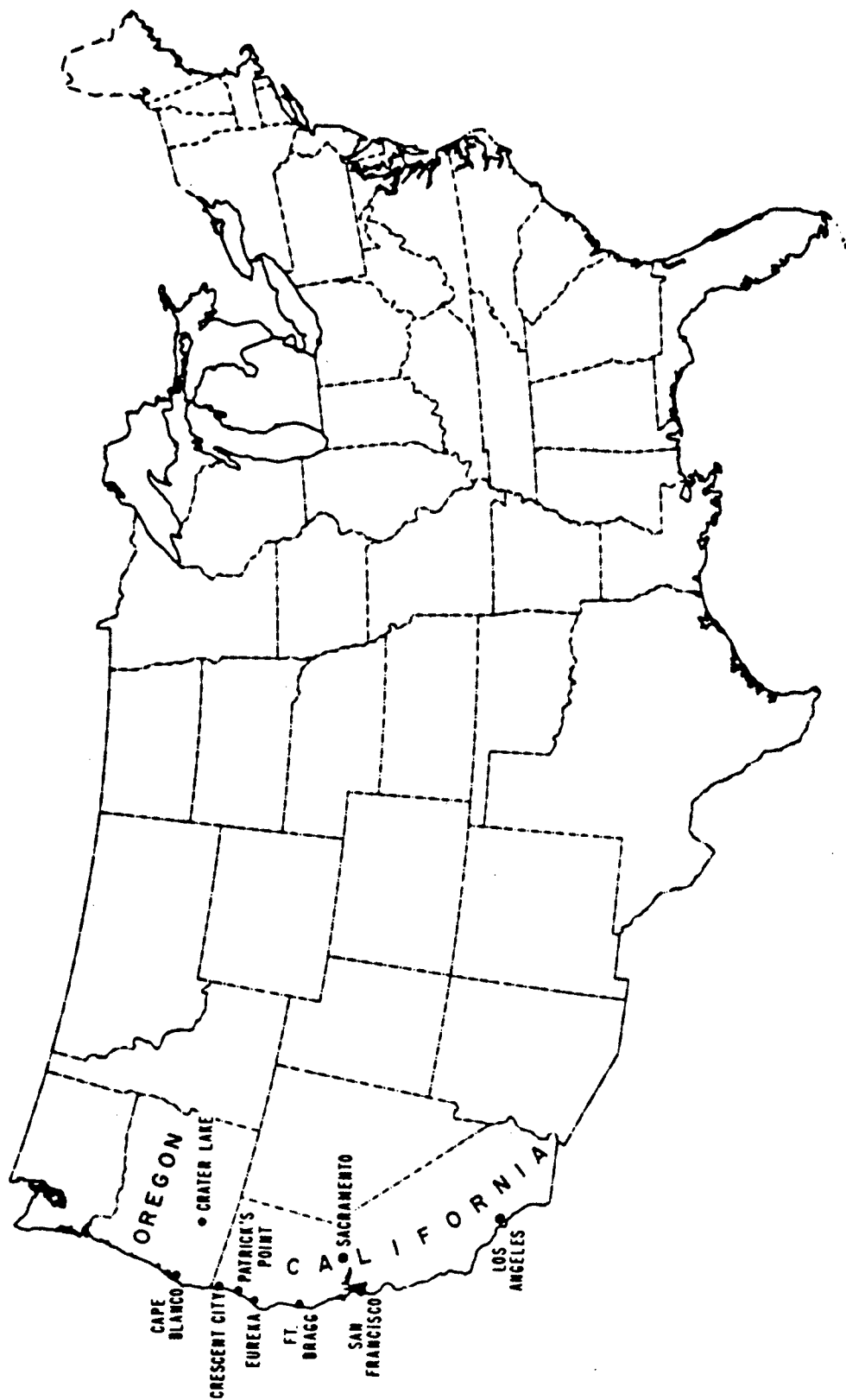
In order to have a fair coverage of synoptic weather conditions, we planned two field sampling trips, each of about 14 days. The first trip covered the period of September 25 to October 6, 1965, and the second the period of October 28 to November 9, 1965.

Three sampling sites were used during these periods--Crater Lake National Park, Oregon; Patrick Point State Park, California; and Cape Blanco, Oregon. These locations are shown on the area map in Fig. 1.

Crater Lake National Park was used for sampling higher altitude air mass conditions. Figure 2 is a detailed map of the sampling area. As the figure shows, the actual sampling site was at an altitude of 2200 meters on the western portion of the summit of Mt. Mazama, within which is Crater Lake. The sampling area was not influenced by the local traffic in the park. Since the area west of this site to the Pacific Ocean is sparsely populated and heavily wooded, the Pacific air masses can be expected to pass the 100 miles from the coast with very little chemical modification from urban effects. Figure 3 shows the Crater Lake site and a closeup of the instrumentation trailer at the site during the first test period.

During the first trip coastal samples were taken in Patrick Point State Park, 30 miles north of Eureka, California. The sampling location was about 45 meters above sea level on Abalone Point, which protrudes into the Pacific at this location. This location did not prove to be especially satisfactory, because in strong winds the spray from the surf affected our measurements. Fog and heavy stratus also limited the usefulness of this coastal site.

For the second trip we obtained permission to sample at the U.S. Coast Guard Station at Cape Blanco, about 75 miles north of the Oregon-California



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FIG. 1 UNITED STATES MAP SHOWING THE SAMPLING SITES

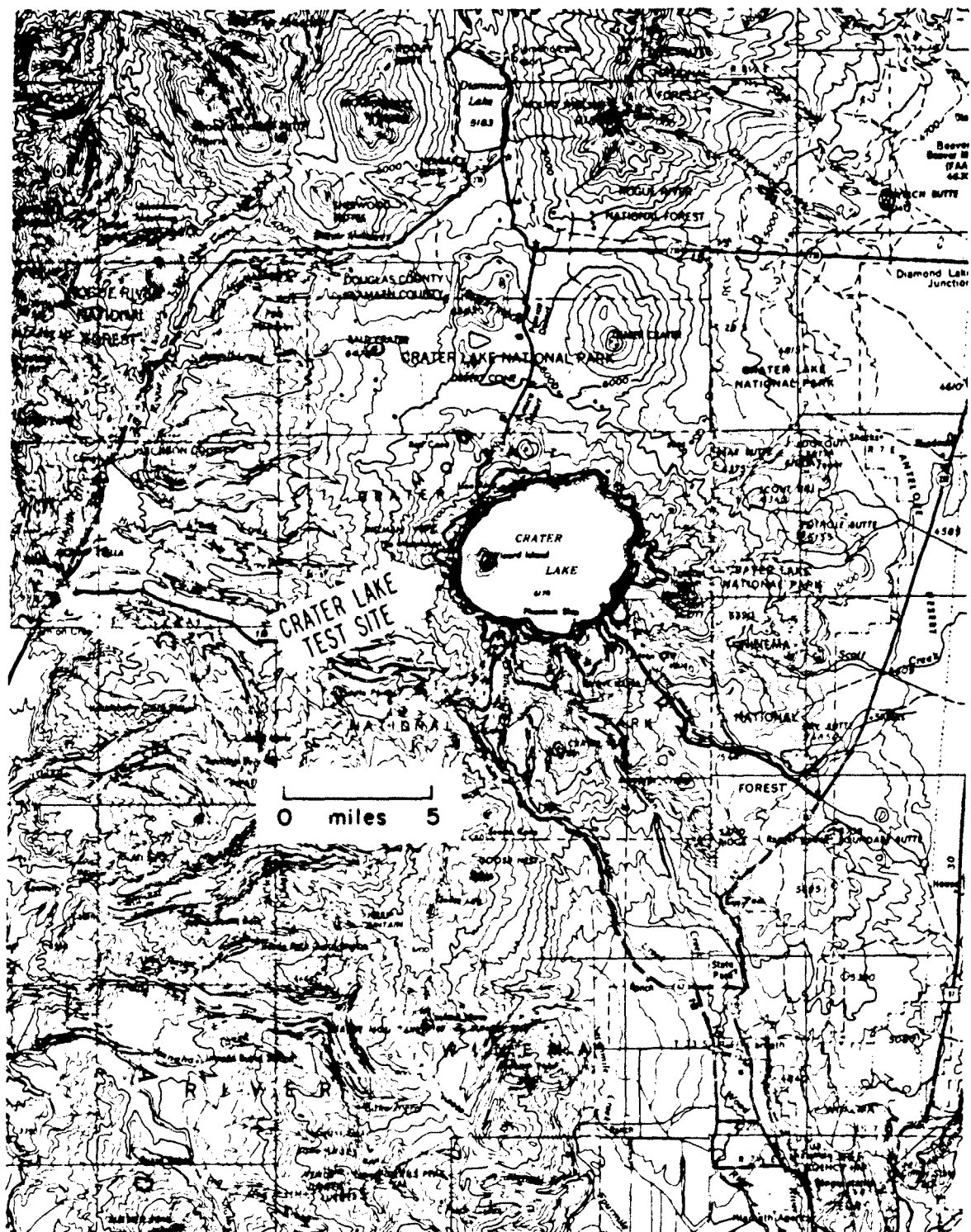


FIG. 2 MAP OF CRATER LAKE AREA

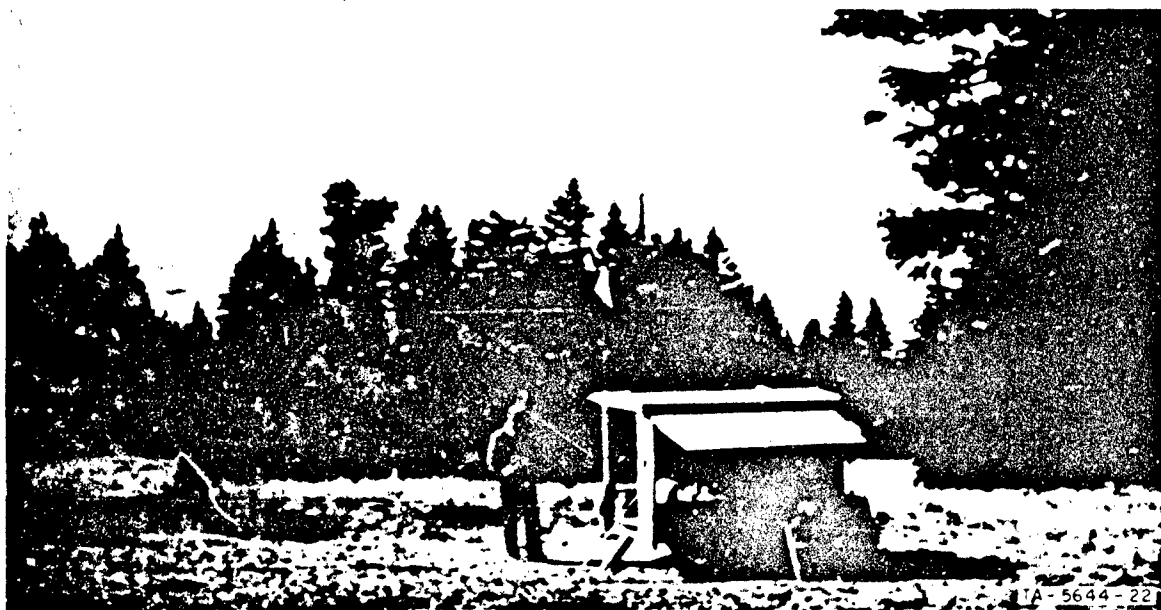


FIG. 3(a) SAMPLING SITE AT CRATER LAKE

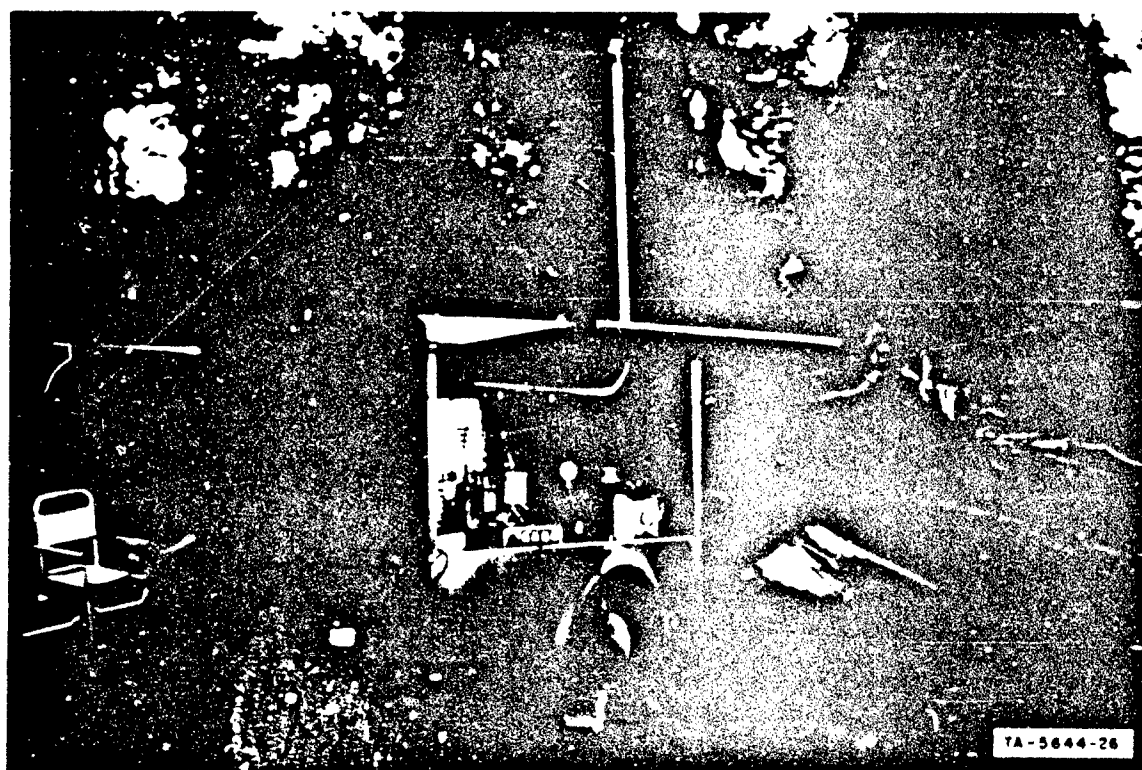


FIG. 3(b) AIR SAMPLING TRAILER AS OPERATED AT CRATER LAKE

border. Figure 4 shows the area of this particular site. Cape Blanco is also one of the stations of the U.S. Public Health Service Air Sampling Network. The sampling point on the Cape Blanco peninsula was 65 meters above sea level and satisfactorily removed from the surf line. It is pictured in Fig. 5.

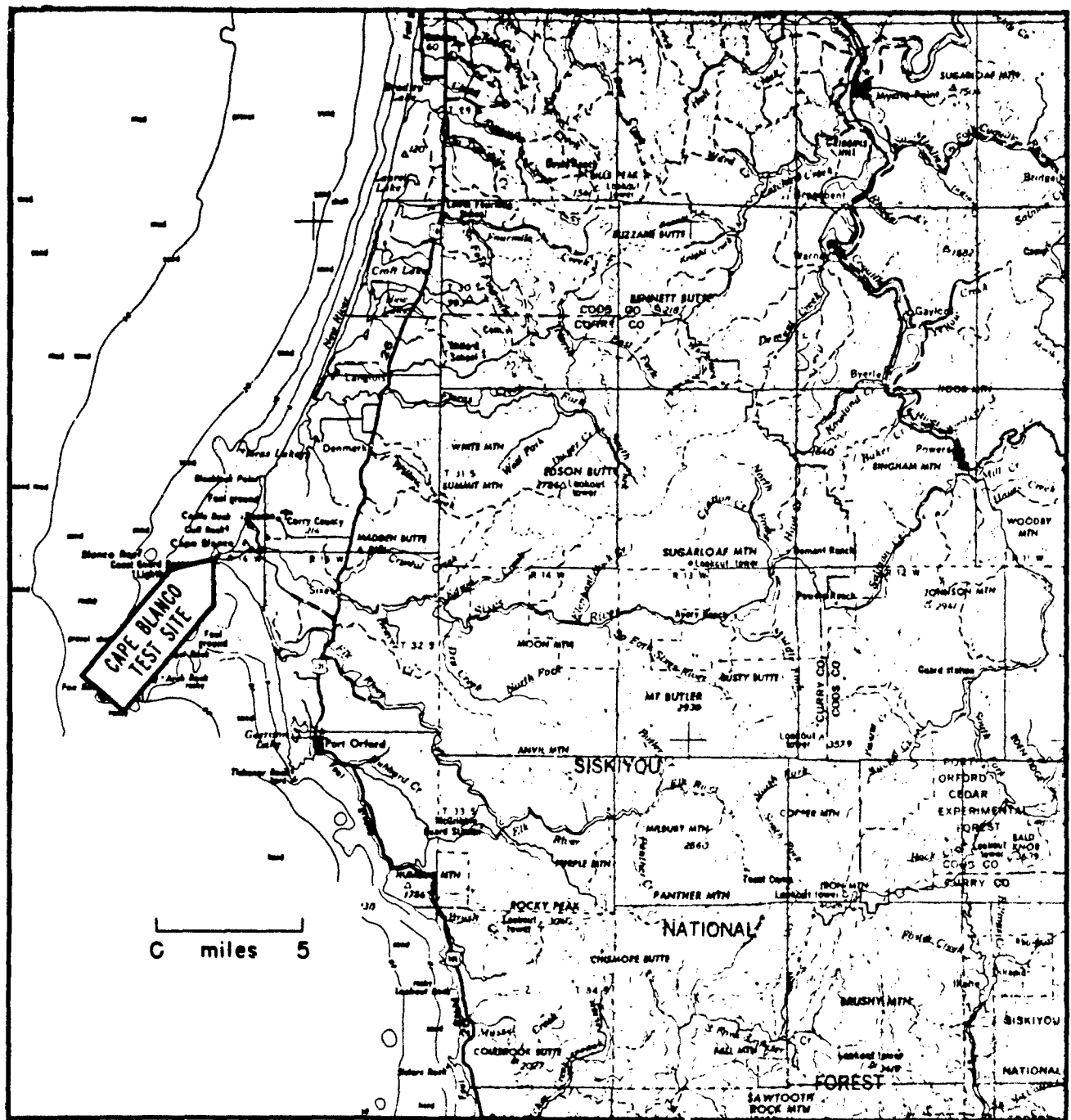


FIG. 4 MAP OF CAPE BLANCO AREA



SOURCE: Oregon State  
Highway Department

FIG. 5 SAMPLING SITE AT CAPE BLANCO



### III INSTRUMENTAL TECHNIQUES

Data on the complete aerosol particle size distribution are very difficult to obtain, because the wide range of sizes and concentrations to be covered requires the simultaneous operation of several methods. However, the combination of a Royco particle counter, Model PC 200 A,\* and an Aitken nuclei counter enabled us to collect information on some of the most important features of the size distribution of natural aerosols. (See Appendix A for a detailed discussion of all instruments used in this study.) The Royco counter measures the light scattered by single particles and gives the size distribution for 15 geometrically arranged size intervals from 0.15 to 4  $\mu$ m radius. For a given optical arrangement the amount of light scattered depends upon the size, shape, and refractive index of the particle in a complex way described by the Mie theory. The counter is calibrated with latex spheres of known size and a refractive index of 1.5. Since the natural aerosol particles do not have a spherical shape nor a uniform refractive index of 1.5, their actual size will differ from the latex sphere equivalent size given by the instrument. However, natural aerosols in clear air masses can be expected to consist of considerable fractions of water soluble compounds, so that the particle shape will be approximately spherical, at least for higher relative humidities, and the refractive index will be close to 1.5. We therefore expect, the Royco data to be fairly representative. Our experience with the Royco counter during the field work was very favorable. The counts are highly reproducible and the variations consistent and in agreement with meteorological and qualitative optical observations.

We used a General Electric nuclei counter, designed by Rich,<sup>†</sup> and during the second field trip we also had a new version of the Scholz

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\* Royco Instrument Co., Inc., Menlo Park, California.

† Small Particle Detector, Type CN, General Electric Co., Schenectady, New York.

counter (see, e.g., Kleinschmidt, 1935). The GE counter is designed for high concentrations and is not very accurate for concentrations of  $1000/\text{cm}^3$  and lower. It is a relative instrument, calibrated against a Pollak counter which is also a relative instrument and which in turn is calibrated against an Aitken nucleus hand counter. The Scholz counter was specifically designed to cover concentrations from less than one hundred to several thousand per cubic centimeter. It is an absolute instrument and in the opinion of the author the best hand counter available for field work. The disadvantages of this instrument are that it takes some time to obtain data and that it is somewhat tedious to use.

Numerous comparisons between the two instruments were made during the field work, and the results are given in Fig. 6. The scatter of the data is considerable, although each value for the Scholz counter was the average of ten single counts and for the GE counter of about five individual readings. It is difficult to estimate to what degree the scatter is due to the statistics of the readings or to actual fluctuations of the aerosol concentrations, since the measurements with the two instruments were not strictly simultaneous. The solid line in Fig. 6 was used for conversion of the more numerous GE counts during our field work.

Particle size distributions of particles smaller than  $0.15\text{ }\mu\text{m}$  radius from clean air masses would be of great interest. Presently such data do not exist. A condensation nuclei counter gives the total concentration covering the whole size range from about  $3 \times 10^{-3}$  to about  $1\text{ }\mu\text{m}$  radius, but no detail as to the size distribution. Any attempts to obtain size distribution data from measurements of the super-saturation spectrum with a more sophisticated nucleus counter remain very dubious. Under normal atmospheric conditions the number of particles larger than  $0.1\text{ }\mu\text{m}$  is small compared with the total concentration, so that for all practical purposes the condensation nucleus concentration is identical with the concentration of aerosols with  $r \leq 0.1\text{ }\mu\text{m}$ .

The aerosol size distributions of sulfate and chloride fractions obtained in this program are based on a sampling system using the Goetz aerosol spectrometer (A.S.) (Goetz et al., 1961), microcoulometric analysis

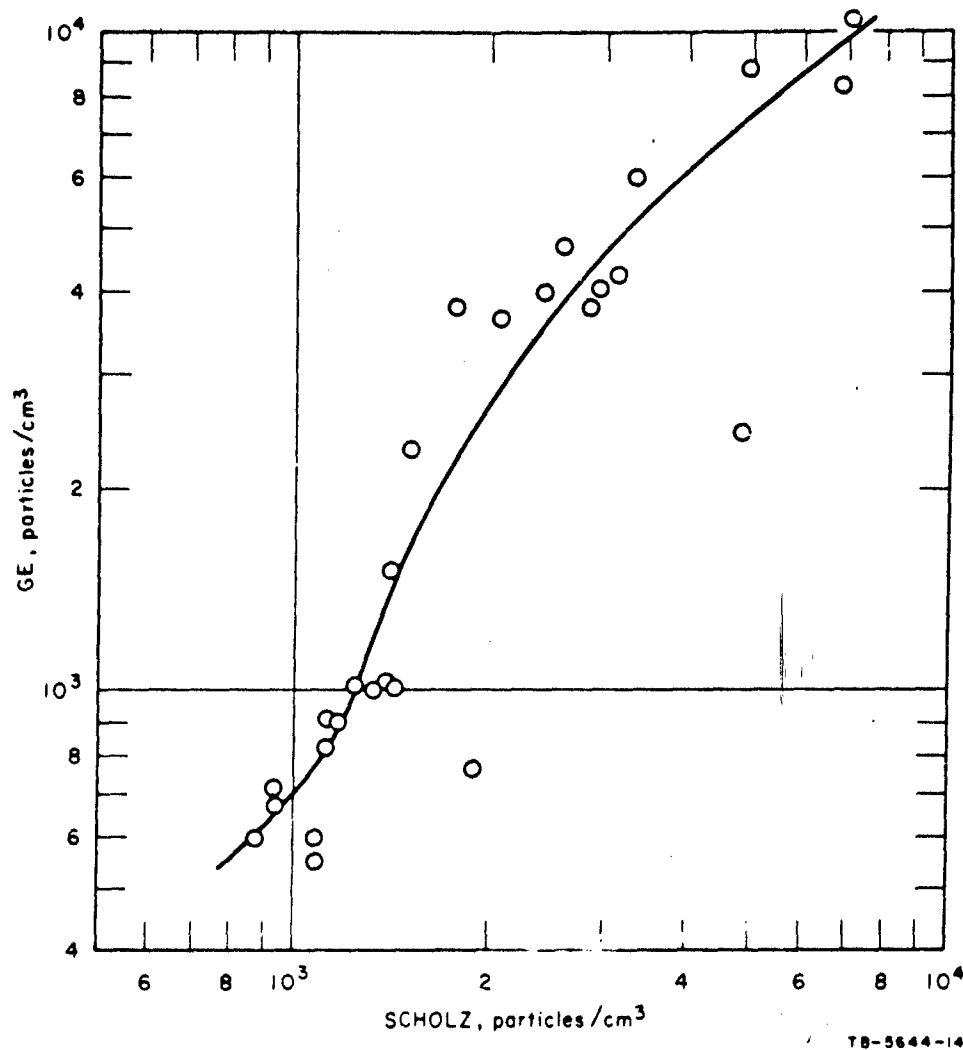


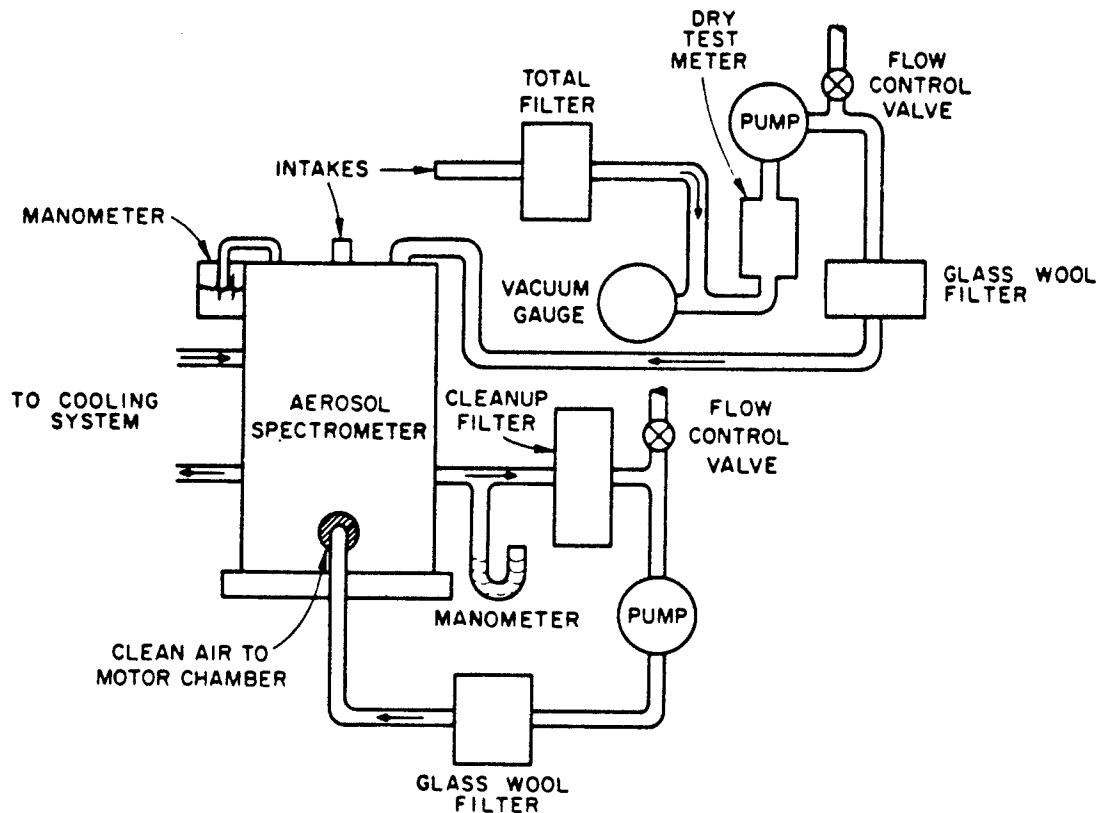
FIG. 6 COMPARISON BETWEEN GE AND SCHOLZ COUNTERS.  
The solid line is the average used for conversion of GE values  
to actual concentrations.

of fractional portions of the collected material for sulfur and chloride, and on a data interpretation system which relates the pattern of mass deposition within the instrument and the uncollected amount passing through the A.S. to the aerosol size distribution (Ludwig and Robinson, 1965).

Briefly, the Goetz aerosol spectrometer consists of a centrifuge which collects the airborne particulate material and a console which controls and monitors the operation of the centrifuge. A cooling system is also used to maintain centrifuge temperature near ambient.

Figure 7 shows schematically the arrangement of the A.S. as it was used in this program. The flow through the cleanup filter, which collects all the material which was not collected in the centrifuge, is adjusted to be the same as the pumping rate of the A.S. Total aerosol samples were also collected with separate filters in parallel with the A.S. These are referred to here as "total" or "filter" samples.

In this program, 0.001-inch-thick stainless steel shim stock was used for the A.S. collection surfaces. Glass fiber filter discs without organic binder were used for total sample and cleanup filter collections.



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FIG. 7 DIAGRAM OF THE ARRANGEMENT OF THE GOETZ AEROSOL SPECTROMETER USED IN THIS PROGRAM

Checks of these filters showed them to have better than 99% collection efficiencies for very small particles at flow rates similar to those used in operation of the equipment. For purposes of analysis their efficiency was assumed to be 100%. Both the glass fiber filters and the stainless steel collection surfaces were carefully washed and dried before use to remove as much background sulfur as possible. The filters and linings were washed in large batches, and the background appeared to be relatively constant through any one batch.

Both sulfur and chloride determinations are described in detail in the appendices. Briefly, the methods are based on microcoulometric titration procedures. Chlorides or halides were titrated directly, while sulfates were determined by converting the sulfates to hydrogen sulfide which was determined by microcoulometric titration.

Size distributions of sulfates and halides were obtained from the mass distribution on the A.S. linings and on the clean-up filter. This calculation followed procedures developed by Ludwig and Robinson (1965). For most samples two sets of total filter concentrations were used to obtain average concentrations for the sampling period and to check the operation of the A.S.

All of the instrumentation was carried and, except for the nucleus counters, operated in the 2 x 1.4-meter covered trailer shown in Figure 3. Three sides of this trailer opened to permit easy operation of the instrumentation. During the second trip the aerosol sampling instruments operated from a common inlet, a 2.5-cm tube which extended 1 meter above the trailer roof. This common inlet was added after the first trip because there was some question as to whether local ground dust could be an adverse influence in the sampling data. In retrospect, it does not seem to have caused a problem.

Power for operating the equipment was obtained from a portable gasoline motor generator at Crater Lake and from available power lines at Patrick Point and Cape Blanco. The generator was placed some distance away and downwind from the trailer to prevent the exhaust from influencing the collected data.

## IV TOTAL AEROSOL SIZE DISTRIBUTIONS

### A. Data Presentation Techniques

To obtain satisfactory summaries of the size distributions of the total aerosol, we converted the Royco data to spectral densities in the form  $dN/d \log r$ ,  $N$  being the total number of particles smaller than radius  $r$  (see, e.g., Junge, 1963). This presentation has several advantages. First, if  $r$  and  $dN/d \log r$  are plotted on log scales it is possible to cover the large ranges encountered for these two parameters in the atmosphere and, second, the size distribution approaches a straight line for  $r > 0.1 \mu\text{m}$ , indicating a power law.

In order to incorporate the condensation nuclei counts into this representation, we chose the following arrangement: (1) the Royco distribution was extrapolated to the ordinate  $r = 0.1 \mu\text{m}$ ; (2) from the point of intersection a horizontal line was drawn in such a way that the integral below the size distribution curve between  $r = 0.01$  and the upper limit of the Royco distribution was equal to the Aitken count. In most cases this was practically identical to the integral between  $r = 0.01$  and  $0.1 \mu\text{m}$ , so that the nuclei count agrees with the reading of the horizontal line on the  $dN/d \log r$  scale.

This form of presentation is based on the assumption that the size distribution of aerosols, including the Aitken nuclei, is continuous and that the maximum of the number distribution is located between  $r = 0.01$  and  $0.1 \mu\text{m}$ . The lower limit was assumed to be at  $r = 0.01 \mu\text{m}$ .

The channels of the Royco are set according to latex sphere equivalent sizes and cover the ranges shown in Table I.

The concentrations of natural aerosols are such that the Royco instrument can be used without dilution. Depending on the actual concentration, we used a counting time of 1, 3, or 10 minutes for each size interval. At Crater Lake, particularly during subsidence, the concentration of particles larger than  $1.0 \mu\text{m}$  was so low that statistics became poor. For this reason the upper limit of the size distributions

Table I  
CHANNEL CALIBRATIONS FOR ROYCO PHOTOMETER

No. of Channels	Radius Interval, $\mu\text{m}$	Channel	Radius Interval, $\mu\text{m}$	Channel	Radius Interval, $\mu\text{m}$
1	0.16-0.20	6	0.50-0.65	11	1.60-2.00
2	0.20-0.25	7	0.65-0.80	12	2.00-2.50
3	0.25-0.32	8	0.80-1.00	13	2.50-3.20
4	0.32-0.40	9	1.00-1.25	14	3.20-4.00
5	0.40-0.50	10	1.25-1.60	15	>4.00

presented in this report increases somewhat with the general concentration level of the aerosols and does not include the largest size intervals.

#### B. Field Sampling Data--Crater Lake, Oregon

A considerable amount of information was accumulated during both field trips and provides an interesting picture of aerosol conditions at an altitude of 2200 m. Most of these data are plotted in Figs. 8 through 16. All concentrations refer to  $\text{cm}^3$  STP. For the analysis of local synoptic situations and of the origin of air masses, we used our own careful meteorological observations at the sampling site, the radiosonde from Medford, Oregon, the U.S. Weather maps, and trajectories drawn from the U.S. Weather Bureau weather maps at San Francisco airport.

Figure 8 gives daily average distributions for the period September 26 through 30 at Crater Lake. During this time a rather stationary high pressure system was located over the eastern Pacific. At 500 mb a trough extended from Central Canada westward and moved southward over the area and intensified during September 27.

On September 26, at the beginning of the sampling period, the area was under the influence of weak subsidence, but the inversion lifted above the station as the influx of air from the north, accompanying the northward-moving trough, became more pronounced. The following two days, September 27 and 28, were characterized by continued influx of cold air from the north. During both of these days the particle concentration

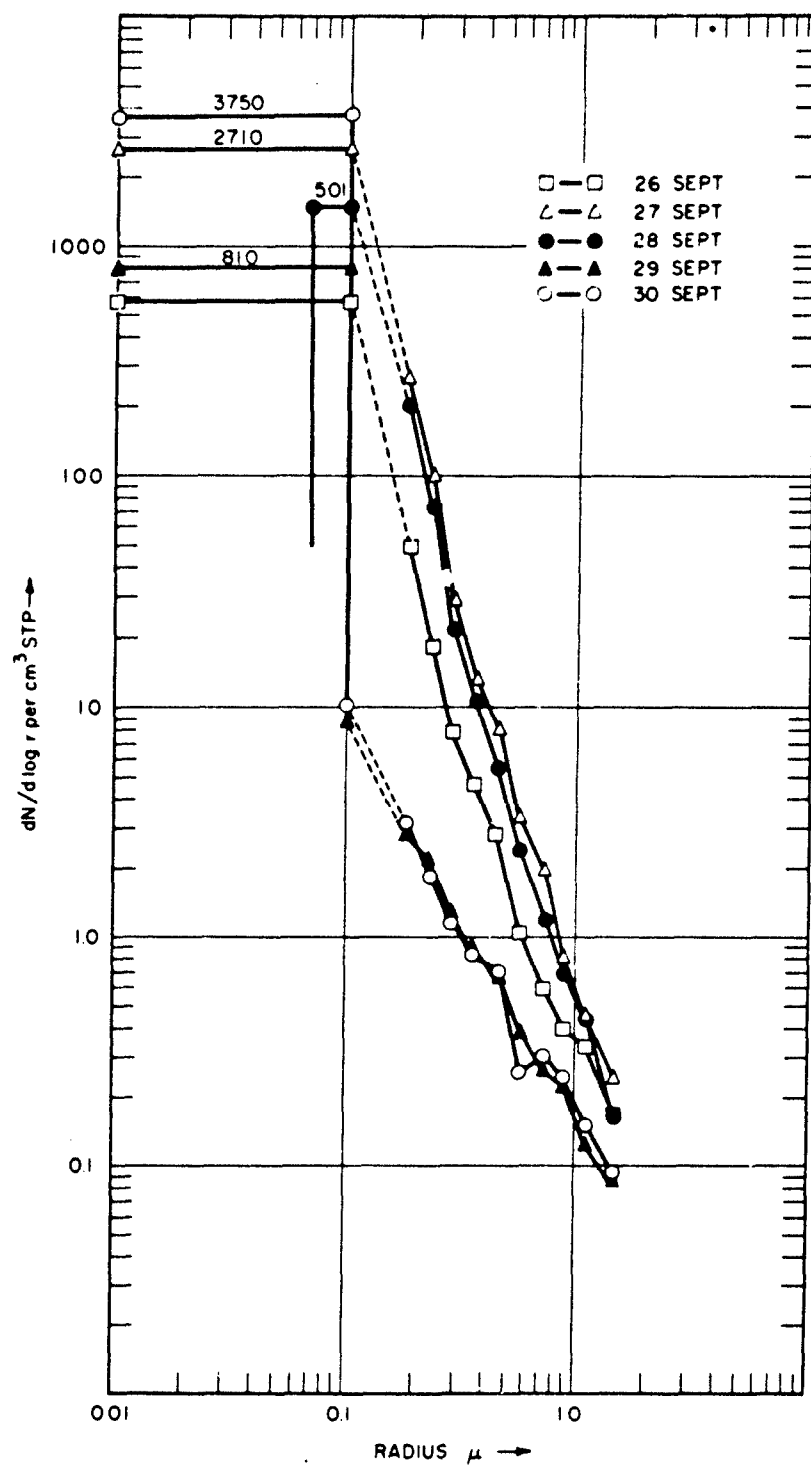


FIG. 8 SIZE DISTRIBUTION OF AEROSOLS, CRATER LAKE,  
DAILY AVERAGE VALUES, FIRST FIELD TRIP, SEPTEMBER 26-30



between  $r = 0.15$  and about  $0.3 \mu\text{m}$  decreased during the day and increased during the night--during the night of September 27 by a factor of 3 to 4, and the night of September 28 by a factor of about 2. However, the concentration of the larger particles remained fairly constant. Despite these variations the average concentration for both days comes out almost identical, indicating the presence of the same general air mass, in agreement with the synoptic situation.

After passage of the trough the sampling area came under the influence of strong subsidence on September 29 and 30 which was caused by an extension of the Pacific high toward the east. The subsidence inversion was well below the sampling station and the visibility was very good, 100 miles or more. The size distribution was rather constant all the time, and this is reflected by the almost identical distributions in Fig. 8 for these two days. Only during the afternoons was there some increase in the small particle size range, probably due to some upslope mixing with air from below the inversion at the time of maximum convection. Except for one more day during the second field trip (October 28), these were the lowest concentrations encountered during our field work. The particle distribution was quite different from those of the other synoptic situations encountered. We believe that they represent to a significant degree the aerosol conditions of the upper troposphere.

All five distributions of Fig. 8 can be well presented by a power law, i.e., by a straight line of the form

$$\frac{dN}{d \log r} = C \left( \frac{r}{r_0} \right)^{\nu^*}$$

with the exponent  $\nu^*$  varying between 1.7 and 3.5;  $r$  is a suitable reference radius, e.g.,  $r_0 = 0.1 \mu\text{m}$ , and  $C$  is the spectral concentration  $dN/d \log r$  for  $r = r_0$ .

The concentrations of the Aitken nuclei during these periods were rather high for air masses of maritime origin, and there is no obvious correlation of their variation with the synoptic situation. One might think that the Aitken nuclei concentration is more sensitive to any

influence during the passage over land before arrival at the sampling stations than is the particle size range covered by the Royco. This would agree with the earlier observation that for the Royco data the smallest particles showed the strongest variations, e.g. on September 27 and 28. However, as is shown below, the Aitken nuclei concentrations at Crater Lake are on the average even lower than at the coastal stations, so that the land influence cannot be very large.

Figures 9 to 12 give data taken at Crater Lake during the second field trip. In order to show the daily variations in more detail we have averaged the counts for periods of 1 to 2 hours for a number of individual days in Figs. 10 to 12. There are distinct differences from day to day, but changes during a given day are slow and fairly systematic. In most cases the deviations from a power law are small, but  $v^*$  itself shows some variation. There is the tendency for the distributions to be concave for larger particle sizes, e.g. in Figs. 10 and 11, but not always. In a few cases there are stronger deviations from the power law, e.g. Fig. 9, October 28, which is a case of subsidence similar to September 29 and 30.

We would like to draw attention to the fact that the concentration of particles of about  $1 \mu\text{m}$  and larger varies surprisingly little for all Crater Lake data. Whereas the concentration of  $0.2 \mu\text{m}$  particles fluctuates by a factor of a hundred (minimum values September 28 and 29 and October 28, maximum values October 29 and November 2), the  $1 \mu\text{m}$  particles fluctuate only by a factor of ten (minimum value October 28, maximum values November 1 and 2). This tendency for the larger particles to be the more conservative components of the natural aerosols agrees with experience from other locations. The more erratic variations at the extreme upper end of the distribution are believed to be the result of poor statistics, because the total counts for channels 10 and 11 were always in the range of 1 particle per minute.

During this period the weather situation showed a high pressure system over the western part of the U.S. with a light to moderate influx of 700 mb of Pacific air from west to southwest and mostly good visibility with varying amounts of high clouds. The subsidence on October 28

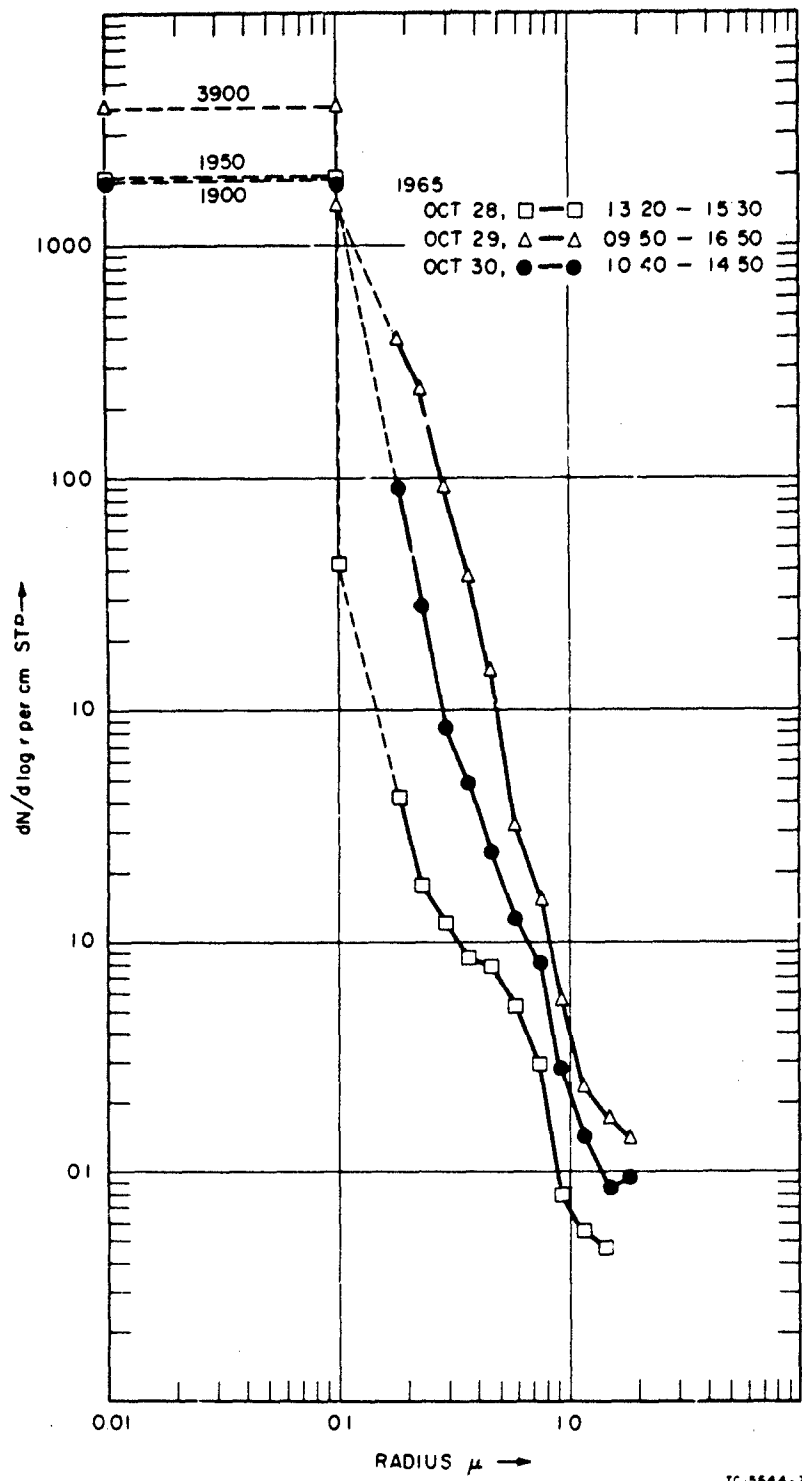


FIG. 9 SIZE DISTRIBUTION OF AEROSOLS, CRATER LAKE, OCTOBER 28 TO 30

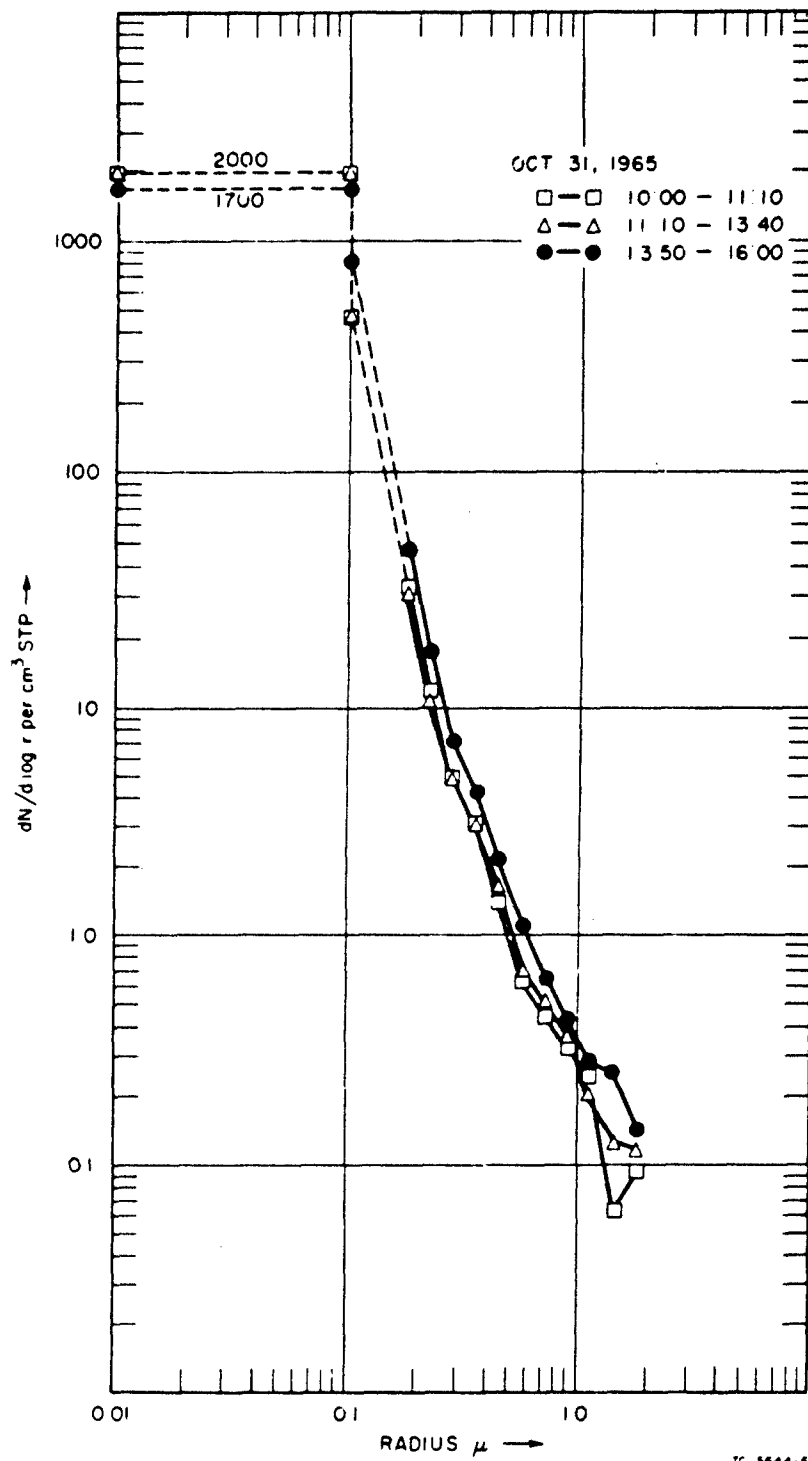


FIG. 10 SIZE DISTRIBUTION OF AEROSOLS, CRATER LAKE, OCTOBER 31

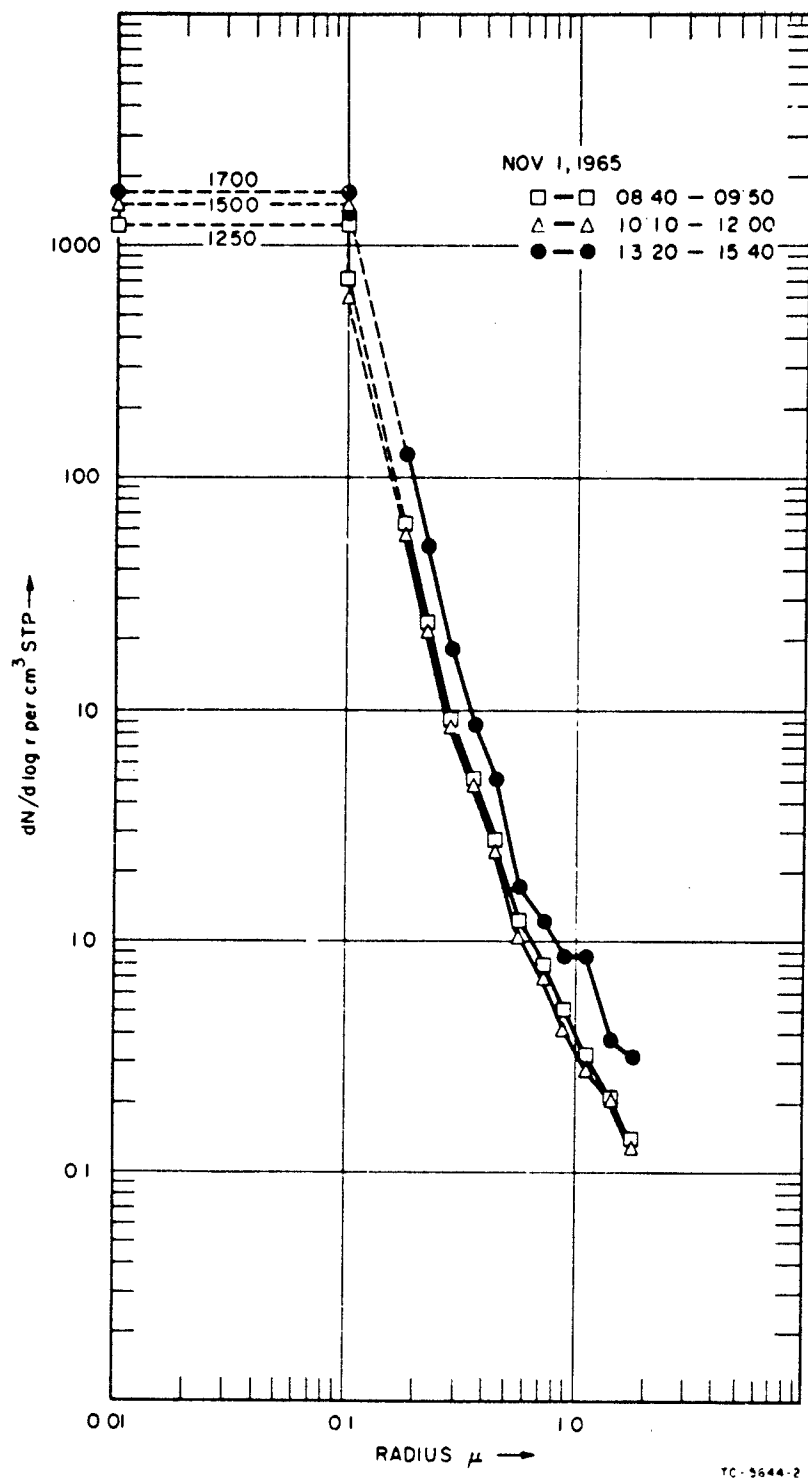


FIG. 11 SIZE DISTRIBUTION OF AEROSOLS, CRATER LAKE, NOVEMBER 1

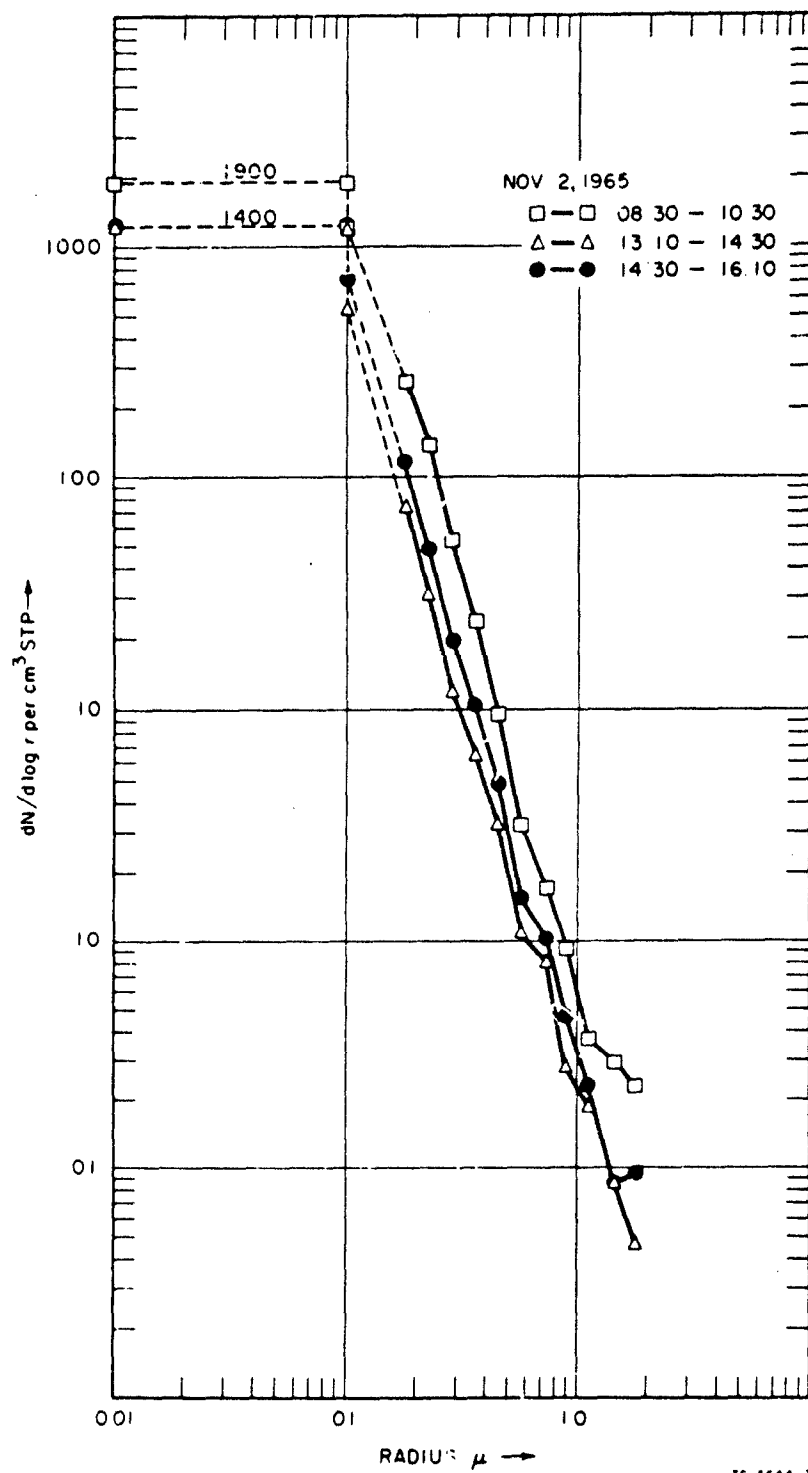


FIG. 12 SIZE DISTRIBUTION OF AEROSOLS, CRATER LAKE, NOVEMBER 2

occurred after passage of a cold front from the west. For the other days the difference in origin of the air masses does not seem to be very pronounced, and this agrees with the fact that the size distributions, including the Aitken nuclei counts, do not vary too much.

The weather was almost ideal for our purpose, and we feel that the data obtained at Crater Lake during the second field trip are as representative of Pacific air masses at about 2500 meters altitude as can be expected if sampling is done without aircraft support. The trajectories always indicated rather direct maritime origin of the air masses with only a short passage over southern Oregon or northern California.

#### C. Field Sampling Data--Cape Blanco, Oregon

We will not present data from the coast for the first field trip, because there was considerable interference of fog and salt spray from heavy surf at the Patrick Point location.

Sampling at the coast during the second field trip was done at the Coast Guard station on Cape Blanco. The cape, as shown in Fig. 4, protrudes from the coast into the ocean and has a height of 65 meters above sea level with steep cliffs, so that the influence of local surf is reduced to a minimum. The weather during the period of November 5 to 9 was in general characterized by a ridge across our area connecting high pressure systems over northern Central U.S. and off the coast of Mexico. Surface winds at the station were always from south to southwest. They are obviously strongly guided by the steep cliffs of the coast running north-south so that the predominant wind direction is from the south irrespective of considerable variation of the pressure gradient. By drawing the trajectories from the local wind directions, it is therefore not certain whether the air masses actually had some contact with the coast line prior to their arrival at the sampling station. However, on the basis of our other wind and weather observations along the coast, we believe that the data must be considered fairly representative of conditions over the eastern Pacific and that significant local contamination is not represented by the aerosol data.

Figures 13 to 16 give the data for individual days at Cape Blanco. The variations from hour to hour are more pronounced at the coast than at Crater Lake and so are the deviations from a straight line. The concentration of particles larger than about  $0.4 \mu\text{m}$  is higher at Cape Blanco than at Crater Lake, and for this reason we were able to extend the distributions to larger sizes. November 8, 0800-0900, Figure 15, is an exceptional case with a secondary peak around  $r = 0.4 \mu\text{m}$ , but otherwise the concentration increases monotonically with decreasing particle radius.

The Aitken nuclei concentrations are, on the average, higher than at Crater Lake. Perhaps in a few cases contamination from land cannot be excluded, but even in those cases where contamination is extremely unlikely the counts were unexpectedly high for maritime air masses. On November 9 we made a vertical profile of nuclei counts from the lighthouse sampling site to the edge of the water 65 meters below to see if there was any nuclei production from the surf, which was at that time, however, not strong. There was no difference in nuclei concentration between the surf area and the lighthouse. We have to accept these higher nuclei concentrations, therefore, as representative of maritime surface air masses during our sampling period.

#### D. Discussion of Total Aerosol Size Data

In order to obtain reasonably representative distributions for Pacific air masses, we have combined the data into three groups:

1. Crater Lake, strong subsidence, September 29 and 30, and October 28
2. Crater Lake, except subsidence
3. Cape Blanco, all data

In Figs. 17 and 18 we have plotted the arithmetic and geometric mean distributions for groups 2 and 3; the standard geometric deviations are also shown. The difference between the two means in both cases is negligible. The standard geometric deviation is rather constant over the whole range and is of the order of 1.5 to 2.0, except for the upper end of the distribution where it increases due to the previously mentioned statistical sampling problems.



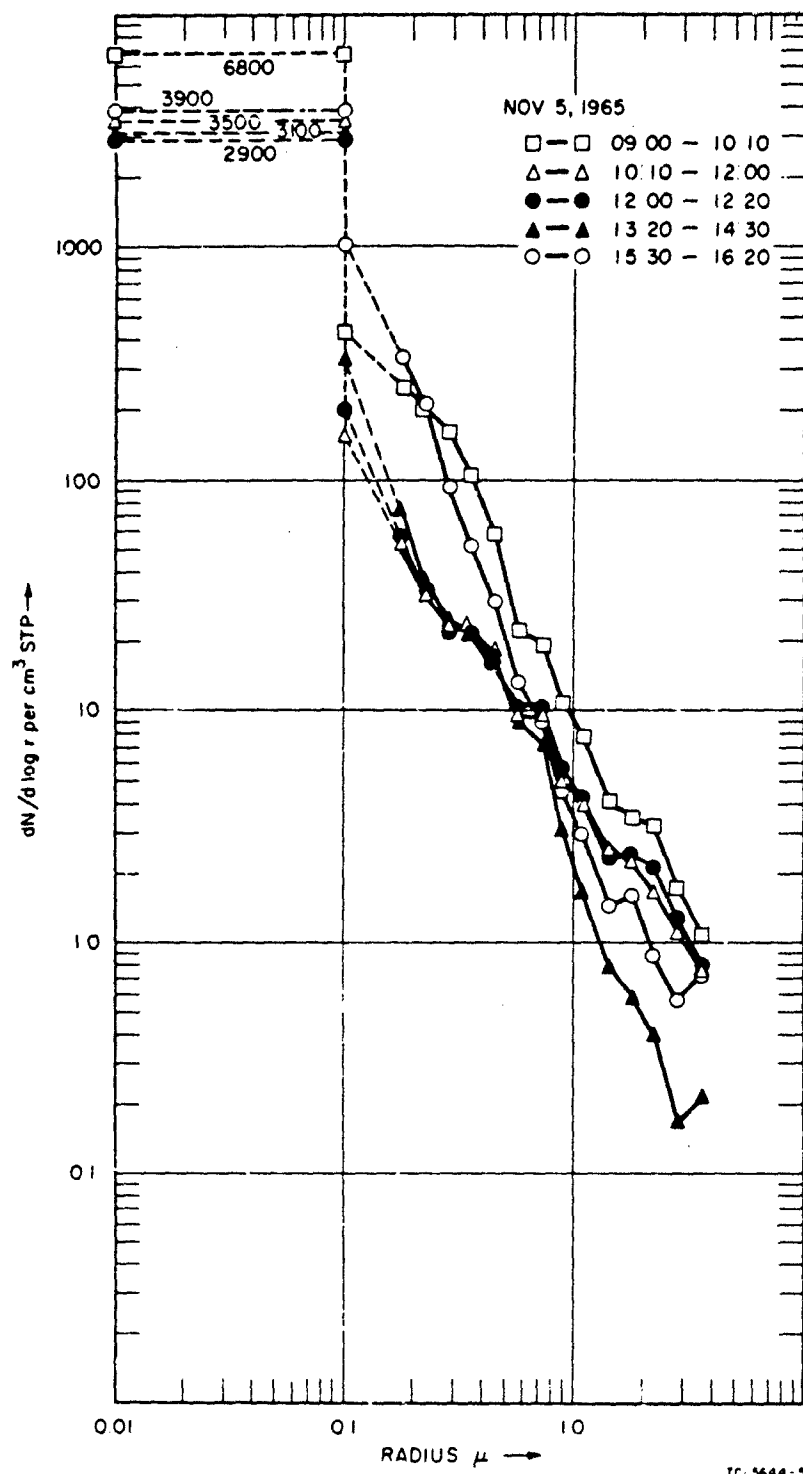


FIG. 13 SIZE DISTRIBUTION OF AEROSOLS, CAPE BLANCO, NOVEMBER 5

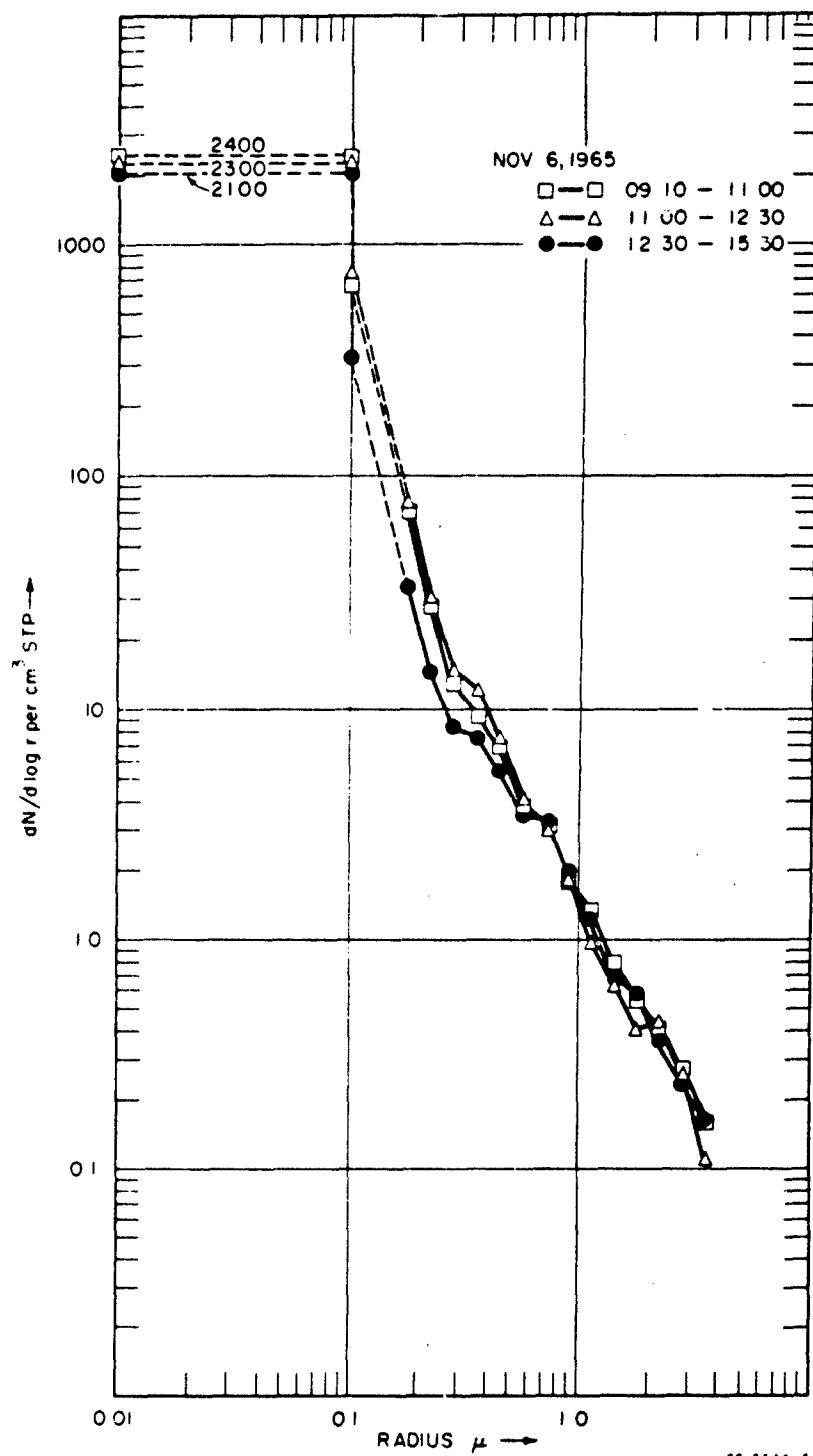


FIG. 14 SIZE DISTRIBUTION OF AEROSOLS, CAPE BLANCO, NOVEMBER 6

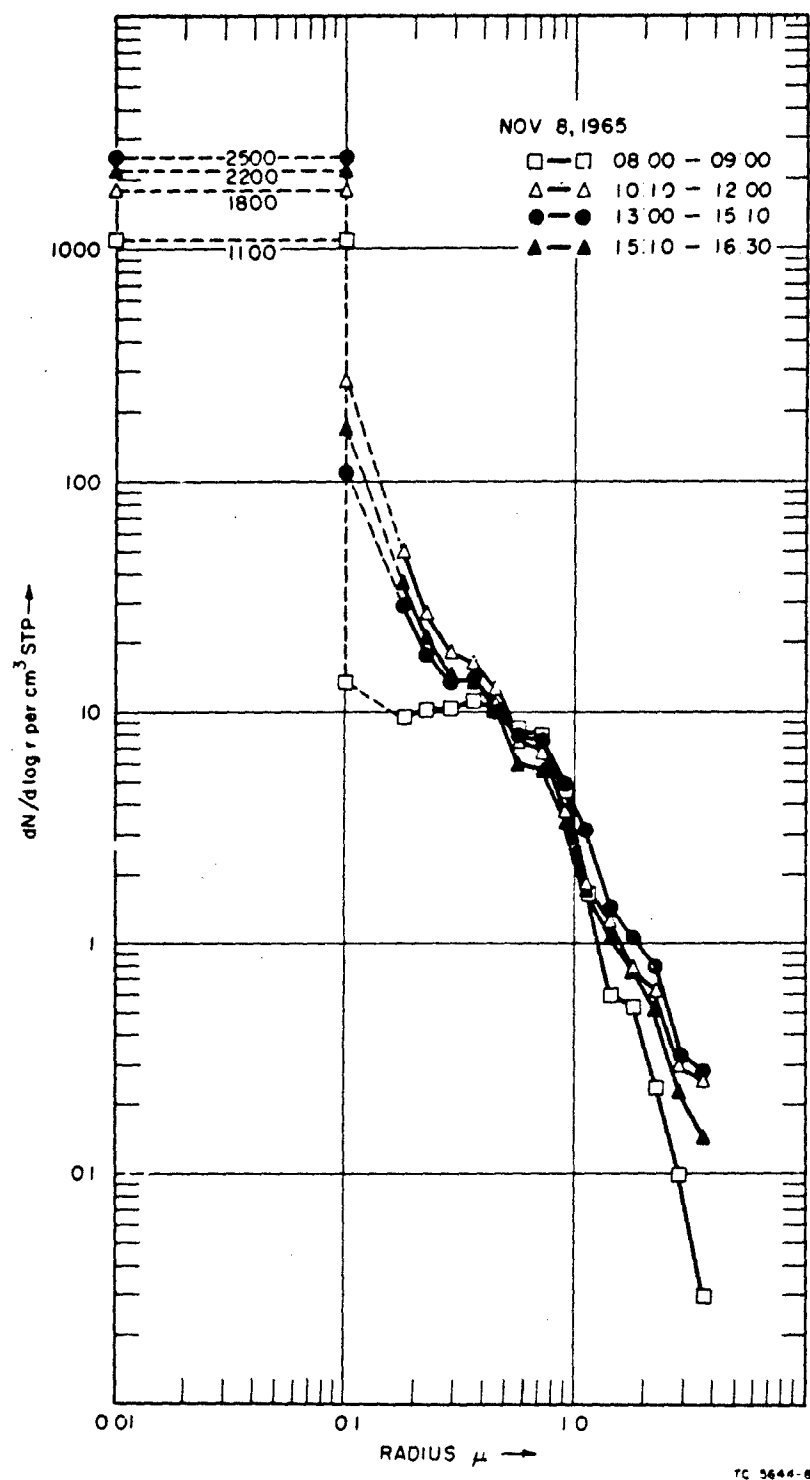


FIG. 15 SIZE DISTRIBUTION OF AEROSOLS, CAPE BLANCO, NOVEMBER 8

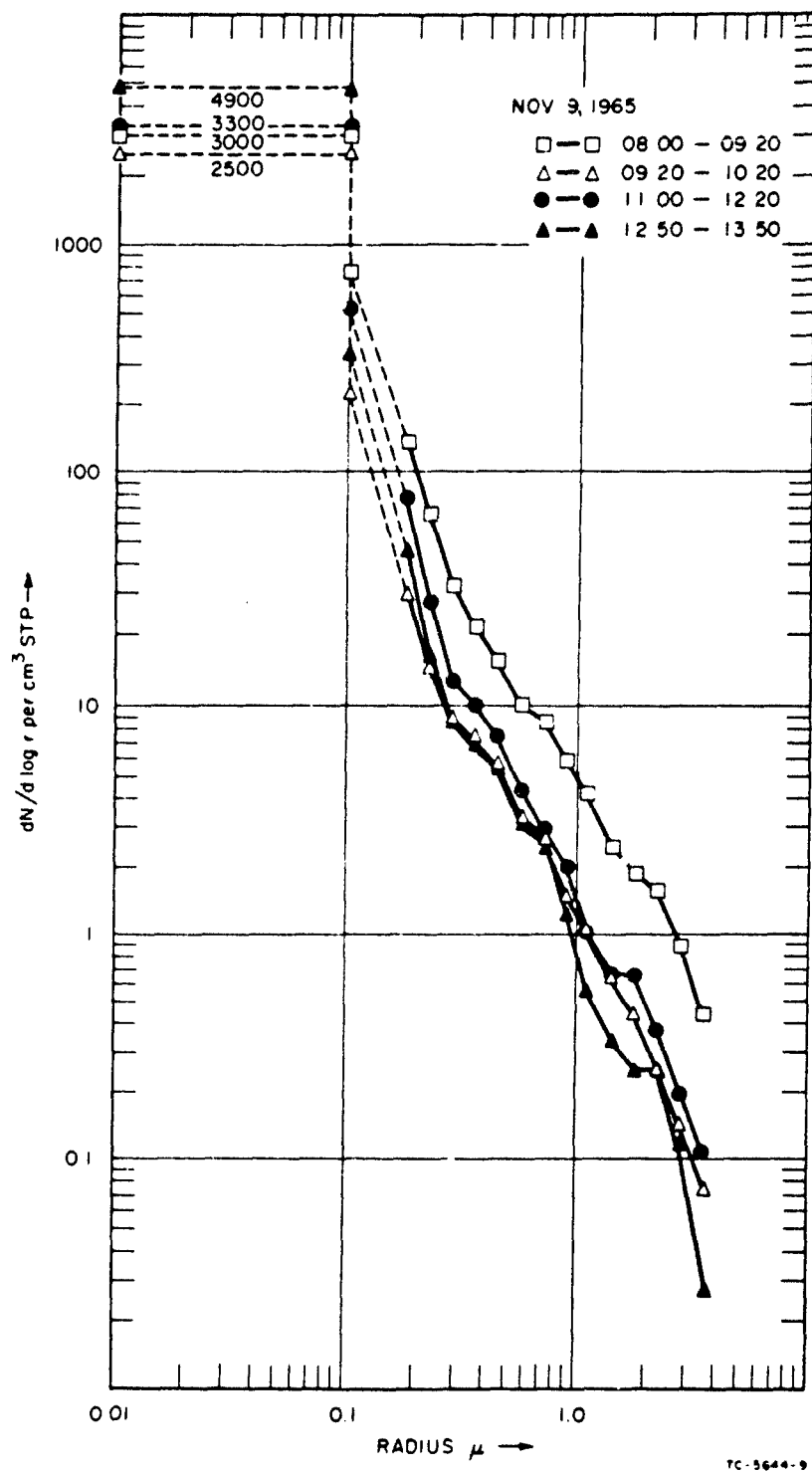


FIG. 16 SIZE DISTRIBUTION OF AEROSOLS, CAPE BLANCO, NOVEMBER 9

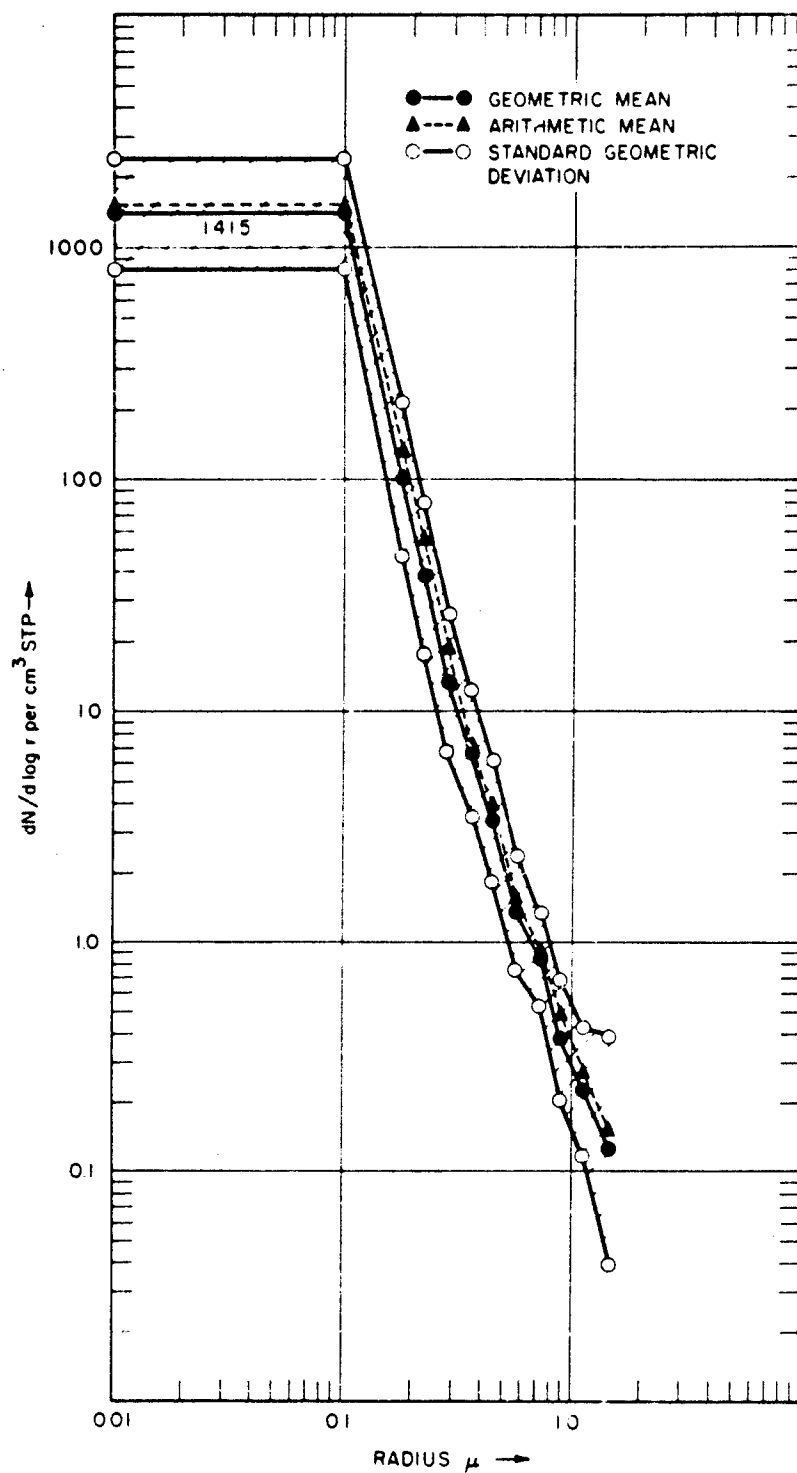
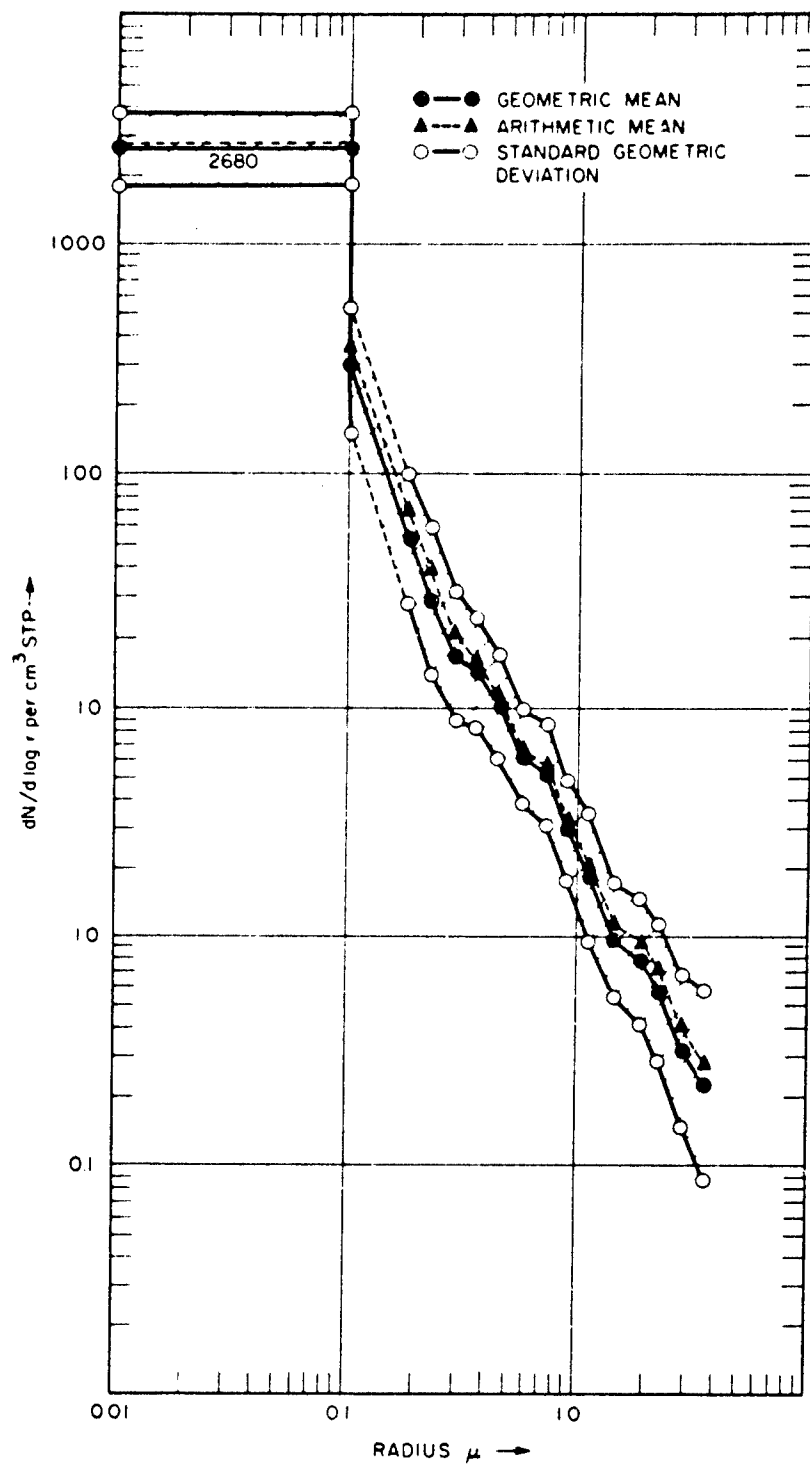


FIG. 17 GEOMETRIC AND ARITHMETIC MEAN SIZE DISTRIBUTIONS OF AEROSOLS FOR ALL CRATER LAKE DATA, EXCLUDING SUBSIDENCE



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FIG. 18 GEOMETRIC AND ARITHMETIC MEAN SIZE DISTRIBUTIONS OF AEROSOLS FOR ALL CAPE BLANCO DATA

In Fig. 19 the average distributions of all three groups are compared. The Crater Lake "except subsidence" distribution is closest to a straight line with  $v^* = 3.2$ . The two other groups show larger deviations and irregularities and a value of  $v^*$  close to 2. Groups 2 and 3 can be expected to represent Pacific air masses fairly well at two different altitudes, and it is not unreasonable to assume that the differences may be due to a sea spray component in the Cape Blanco data. Although the data at both places were obtained during different periods, they can be regarded as sufficiently representative to justify such comparison.

The concentrations for  $r = 0.2 \mu\text{m}$  are almost the same, but at larger sizes the Cape Blanco concentrations are definitely higher. It is quite interesting to note that the difference between the two curves plotted in Fig. 19 is almost identical in shape and concentration with the average sea spray distribution suggested by the author on the basis of data obtained by Woodcock, Metnieks, and others (Junge, 1963, Fig. 26). At Cape Blanco the influence of local surf was eliminated to a large extent by the location of the sampler, so that the sea spray component of the Cape Blanco data is probably fairly representative of average surface conditions in Pacific air masses. The fact that there is such a pronounced difference between the Cape Blanco and the Crater Lake distributions strongly suggests that the sea spray aerosol in Pacific air, at least during the period of our field trips, was restricted to a rather shallow layer of about 2 km or less. These findings are in agreement with vertical distributions found by Woodcock in trade wind areas (see, e.g., Junge, 1963, Fig. 24). As we will see later these observations are also fully supported by the  $\text{Cl}$  concentrations found for Crater Lake and Cape Blanco aerosols. A more detailed discussion of all these data will be presented in the discussion of the chemical data in Section V.

A few remarks should be added about the concentrations of the Aitken particles observed in our studies. Measurements from very remote areas over the ocean, e.g., in low latitudes over the Atlantic Ocean (Lettau, 1939) and over the northeastern Atlantic above 2 km (Day, 1955) indicate particle concentrations in clean air masses of about  $300/\text{cm}^3$ . Such

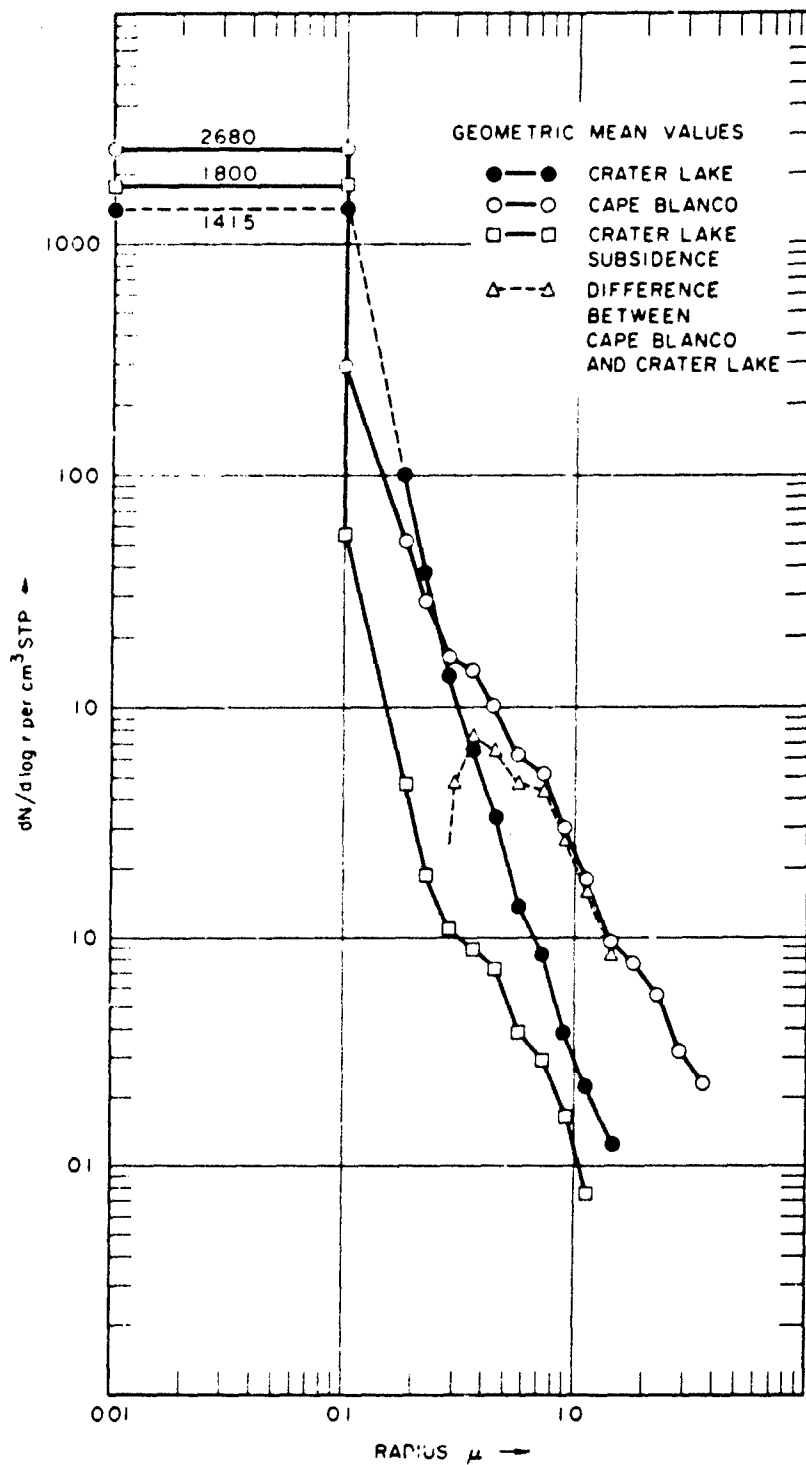


FIG. 19 GEOMETRIC MEAN SIZE DISTRIBUTIONS FOR CRATER LAKE, WITH AND WITHOUT SUBSIDENCE, AND FOR CAPE BLANCO. In addition the difference between Cape Blanco and Crater Lake without subsidence is plotted.



concentrations have also been found above 5 km over the Central U.S. (Junge, 1961). We were therefore rather surprised to find average concentrations between 1000 and 2000/cm<sup>3</sup> at the coast and in most cases also at Crater Lake. Even during subsidence at Crater Lake the concentration did not drop below 700/cm<sup>3</sup>. Aitken profile concentrations at Haleakala presented in Fig. 20 are about 600 (Bullrich et al., 1966). Since our counts are fairly reliable and consistent, this result suggests that air masses over the eastern Pacific at our latitudes may be influenced by some source of Aitken nuclei.

Another point worth mentioning is the fact that the general size distribution of the aerosols as indicated by our simplified presentation suggests strongly that our assumption of a continuous size spectrum from above  $r = 1 \mu\text{m}$  all the way down to sizes of  $r = 0.01 \mu\text{m}$  or even smaller for these air masses is correct. It is very hard to visualize that there is a pronounced dip in the distribution around  $0.1 \mu\text{m}$  as suggested by the results of Goetz et al (1961), who very often found a lower limit of the size distribution around this size in Pacific air with the A.S. It can, of course, not be excluded that this may happen under special geographic conditions, but we do not believe that this is the rule and we think that our present data again support this view.

Finally, we wish to point out that recent measurements (Bullrich et al, 1966) at an altitude of about 3050 m on Haleakala on the island of Maui in Hawaii and above the trade wind inversion gave aerosol concentrations which are similar to those obtained during subsidence at Crater Lake. Figure 20 shows the comparison with our data. The data from Hawaii were obtained using a special impactor, whereas we used the Royco counter. The Aitken nuclei concentration at Haleakala was less than half the value at Crater Lake, but the size distribution for  $r > 0.1 \mu\text{m}$  is indeed in good agreement with our data. These measurements were taken at the observatory on Haleakala, which is located at 3050 meters on Maui, Hawaii, and the distribution is representative of conditions well above the trade wind inversion, i.e., of subsidence. The distribution at Haleakala is the average of 15 measurements during the period August 12 to September 15, 1965. Since these data were obtained during

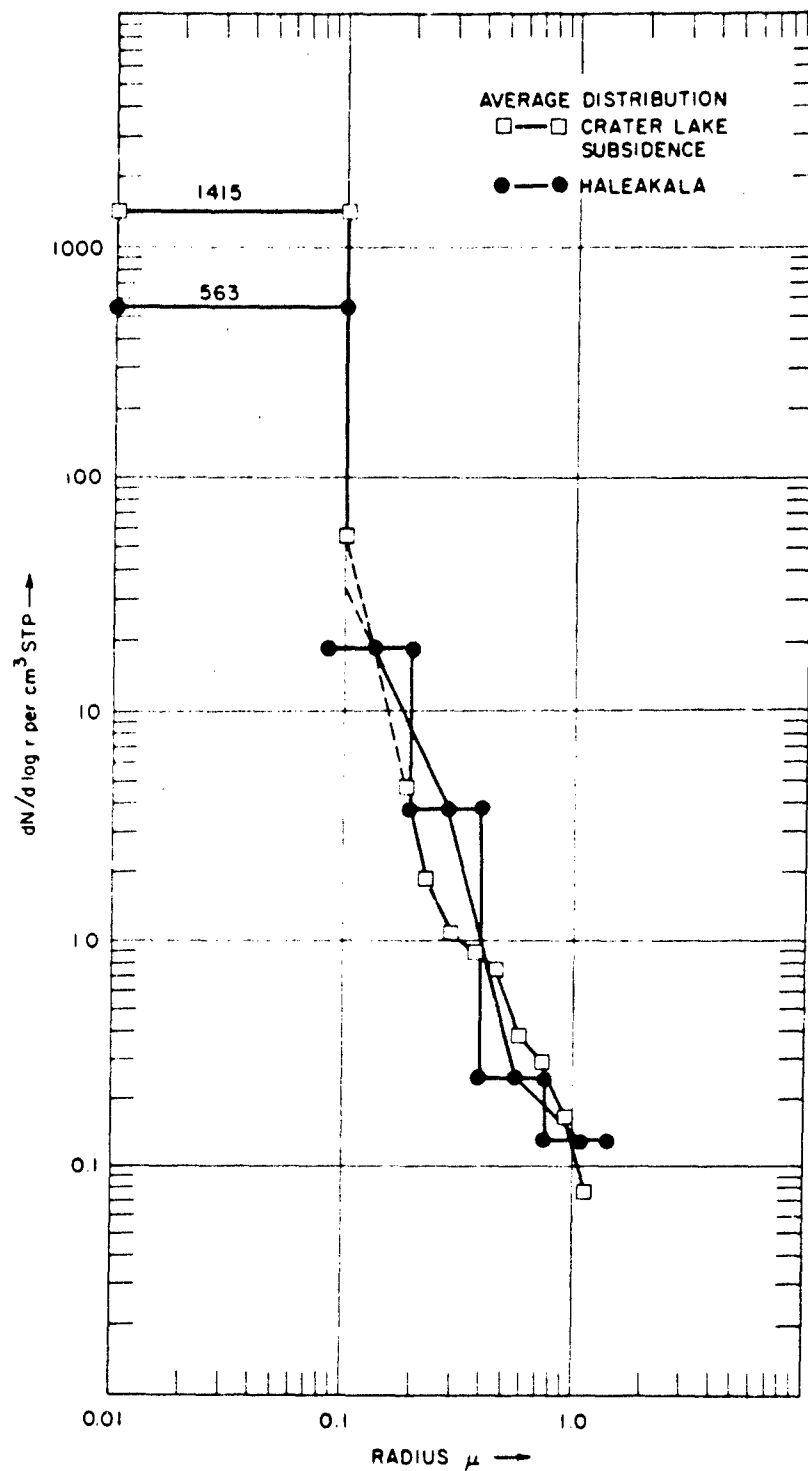


FIG. 20 COMPARISON BETWEEN CRATER LAKE WITH SUBSIDENCE AND IMPACTOR DATA FROM HALEAKALA, HAWAII

day time there is the possibility of some contamination from below the inversion layer, but the same is true for the Crater Lake data. Except for the difference in Aitken particle concentration, the general agreement is remarkable and supports the idea that a rather uniform background aerosol may be representative of the upper troposphere.

## V SULFUR AND CHLORIDE AEROSOL SIZE DISTRIBUTIONS

The main difficulty in obtaining size distributions of sulfur and chloride with the A.S. and backup filters in clean air is the low concentrations encountered and the unavoidable background chemical content of the A.S. linings and the filters. Since no information of this nature was available for Pacific air masses, the first field trip, September 25 to October 6, 1965, served the special purposes of obtaining general information on aerosol concentrations and testing the sampling techniques. This latter was of particular importance, since the methods which were to be used had been developed for use in polluted urban atmospheres where much higher concentrations are the general rule. A preliminary survey of sulfate concentration data from several studies on the West Coast (see Section V-E) indicated sulfate background concentrations of about  $5 \mu\text{g}/\text{m}^3$  which on a sulfur basis is about  $1.7 \mu\text{g}/\text{m}^3$  (Holzworth, 1959; Lodge et al., 1960). However, in our program the levels were only a third to a half these values.

After the first field trip, a careful analysis of the chemical data indicated that the results were unreliable, because the net amount of the samples was frequently too low relative to the lining and filter background, and because there was considerable scatter in the background values. For these two reasons, it was decided to discard the chemical data from the first trip and to make some improvements in the sampling and analysis procedures. Considerable effort was expended to reduce and stabilize the lining and filter background levels (see Appendix A, Section A-6). Briefly, the procedures for cleaning the stainless steel linings was to clean them with an organic solvent, wash them twice in boiling distilled water, and finally centrifuge them to remove the last of the wash water. Clean liners were stored in a sealed jar. Filters were washed twice in boiling distilled water, centrifuged, and oven dried. The result of this extreme care in treating the liners and filters was an average background per segment of the lining of about 0.1  $\mu\text{g}$  sulfur and for the

filters of about one  $\mu\text{g}$  sulfur. Chloride backgrounds were somewhat higher and were about 0.3  $\mu\text{g}$  chloride per liner strip and 1.7  $\mu\text{g}$  chloride per filter.

Because flow rates in the A.S. are fixed, the sampling times had to be lengthened to provide more sample. During the first trip daily samples of about 9 hours were taken with the A.S. system. For the second trip a single sample was extended over several days. This has obvious disadvantages in that the possibility of failure increases because of the small number of samples, and it is difficult to relate the results to specific weather situations because the samples are the integrated results of several days.

As part of the chemical sampling, attempts to measure  $\text{SO}_2$  and  $\text{H}_2\text{S}$  concentrations were also made. The attempts were unsuccessful because of the very low gas concentrations which doubtless were present. However, these gas samplers were preceded by filters to prevent contamination of the gas samples. These filters sampled directly from the air and were not connected to the common inlet used for the A.S. and its parallel total filter. Only the gas sample filters from the Cape Blanco tests were analyzed, and they have proven very important factors in interpreting the A.S. data, as will be pointed out subsequently.

In the tabulations below, the lining samples are broken down into strips, a, b, c, and d. These represent the four strips into which the lining was cut prior to chemical analysis. (See Appendix A, Sect. A-6). The edge of each strip is the locus of an equal travel distance along the A.S. rotor channel and can be identified with a particle size cut-off diameter, i.e., no particles larger than the cut-off size go beyond the given distance down the rotor. The cut-off diameters are also shown in the tables.

#### A. Sulfur Field Data

As mentioned above, we discarded the chemical data from the first field trip; on the second trip we collected only a few samples, but with long sampling times. During this second trip only one sample was collected over the 6-day sampling period at Crater Lake, but it had a

running time of 45 hours. At Cape Blanco two samples of 20 hours each were taken during two periods of three and two days' operation.

The analysis of the field samples gave the following data:

Sample 1: Crater Lake, October 28 to November 2, 45 hours (Table II). A.S. sample volume, 19.6 m<sup>3</sup>.

Total filter sample volume, 44.4 m<sup>3</sup>.

Total S concentration of A.S. and clean-up filter, 0.45 µg/m<sup>3</sup> STP.

Total S concentration of total filter, 0.50 µg/m<sup>3</sup> STP.

Table II  
SULFUR DATA, CRATER LAKE, SAMPLE 1

Section of A.S. Lining	Cut-off Diameter of Section Cuts, µm	Net S Values on Sections after Subtraction of Blanks, µg	Cumulative Net S Values, µg	Cumulative %
a		1.95	8.87	100.0
b	1.70	1.12	6.92	78.5
c	0.82	1.27	5.80	56.8
d	0.48	1.86	4.53	25.2
Clean-up filter	0.26	2.67	2.67	6.3
Total		8.87	8.87	100.0

The agreement between the two total concentrations was considered satisfactory and 0.45 µg/m<sup>3</sup> was accepted as the final value for subsequent calculations.

Sample 2: Cape Blanco November 4 to 6, 20 hours (Table III). A.S. sample volume, 10.5 m<sup>3</sup>.

Total filter sample volume, 26.1 m<sup>3</sup>.

Gas filter sample volume, 16.2 m<sup>3</sup>.

Total S concentration of A.S. and clean-up filter, 0.39 µg/m<sup>3</sup> STP.

Total S concentration of total filter, 0.71 µg/m<sup>3</sup> STP.

Total S concentration of gas sampler filter, 1.08 µg/m<sup>3</sup>.

Table III  
SULFUR DATA, CAPE BLANCO, SAMPLE 2

Section of A.S. Lining	Cut-off Diameter of Section Cuts, $\mu\text{m}$	Net S Values on Sections after Subtraction of Blanks, $\mu\text{g}$	Cumulative Net S Values, $\mu\text{g}$	Cumulative %
a		8.62*	11.39	100.0
b	1.70	0.38	2.77	24.6
c	0.82	0.38	2.39	21.0
d	0.48	0.73	2.01	17.6
Clean-up filter	0.26	1.28	1.28	11.2
Total		11.39	11.39	100.0

\* Corrected to give a total concentration of 1.08 instead of  $0.39 \mu\text{g}/\text{m}^3$  STP.

There is a considerable discrepancy between the three total sulfur concentrations for Cape Blanco; as we will see later, there was also a sizeable discrepancy in the chloride data from Cape Blanco. It seems very likely that the largest particle fraction represented by the sea spray component at Cape Blanco is deposited in the A.S. intake above lining section a and to some degree also in the total filter holder above that filter, but the open filter faces of the gas samplers collect a very high proportion of the large particles. In the total filter holders the filters were partly covered with an intake of 0.3-inch diameter, and this intake was apparently not sufficiently isokinetic for collection of the largest particles. For these reasons we accepted the gas filter concentration as the correct one for the Cape Blanco data. To best calculate an A.S. size distribution, we added to lining section a as much sulfur as was necessary to bring the total concentration of the A.S. plus clean-up filter up to the gas sample filter concentration, i.e., in our case to  $1.08 \mu\text{g}/\text{m}^3$ . Thus the size distribution compensated for the loss of the large particles in the inlet. This procedure was adopted for all Cape Blanco data including both chloride and sulfur calculations.

Sample 3: Cape Blanco, November 8 to 9, 20 hours  
(Table IV). A.S. sample volume, 10.4 m<sup>4</sup>.

Total filter sample volume, 26.2 m<sup>3</sup>.

Gas filter sample volume, 14.4 m<sup>3</sup>.

Total S concentration of A.S. and clean-up  
filter, 0.24 µg/m<sup>3</sup> STP.

Total S concentration of total filter, 0.48 µg/m<sup>3</sup> STP.

Total S concentration of gas filter, 0.69 µg/m<sup>3</sup> STP.

Table IV  
SULFUR DATA, CAPE BLANCO, SAMPLE 3

Section of A.S. Lining	Cut-off Diameter of Section Cuts, µm	Net S Values of Sections after Subtraction of Blanks, µg	Cumulative Net S Values, µg	Cumulative %
a		5.82*	7.25	100.0
b	1.70	0.25	1.43	19.7
c	0.82	0.20	1.18	16.3
d	0.48	0.33	0.98	13.5
Clean-up filter	0.26	0.65	0.65	9.0
Total		7.25	7.25	100.0

\* Corrected to give a total concentration of 0.69 µg/m<sup>3</sup> STP.

It is of interest to compare the ratios of the three total concentrations for both Cape Blanco samples:

Sample 2: 0.39 : 0.71 : 1.08 = 1 : 1.82 : 2.77

Sample 3: 0.24 : 0.48 : 0.69 = 1 : 2.00 : 2.88

The good agreement of these ratios supports the idea that differences in total concentration are caused by differences in collection efficiencies, not by analytical or other errors. The observation that particles larger than about 1 µm radius are not properly collected by the A.S. is of importance for composition studies of aerosols if the A.S. is used and if considerable mass fractions can be expected in this size range.



## B. Discussion of Sulfur Data

The cumulative mass distribution data in the A.S. samples, as corrected for inlet deposition losses, were used to obtain the aerosol size distributions. The computation methods are explained in detail in Appendix A. The results of these computations are plotted in Figs. 21 to 23. From these plots we obtain the comparisons for all of the sulfur data shown in Table V. For consistency we have carried the values to three decimals; although the accuracy of the data does not justify this, it makes comparison of the values easier.

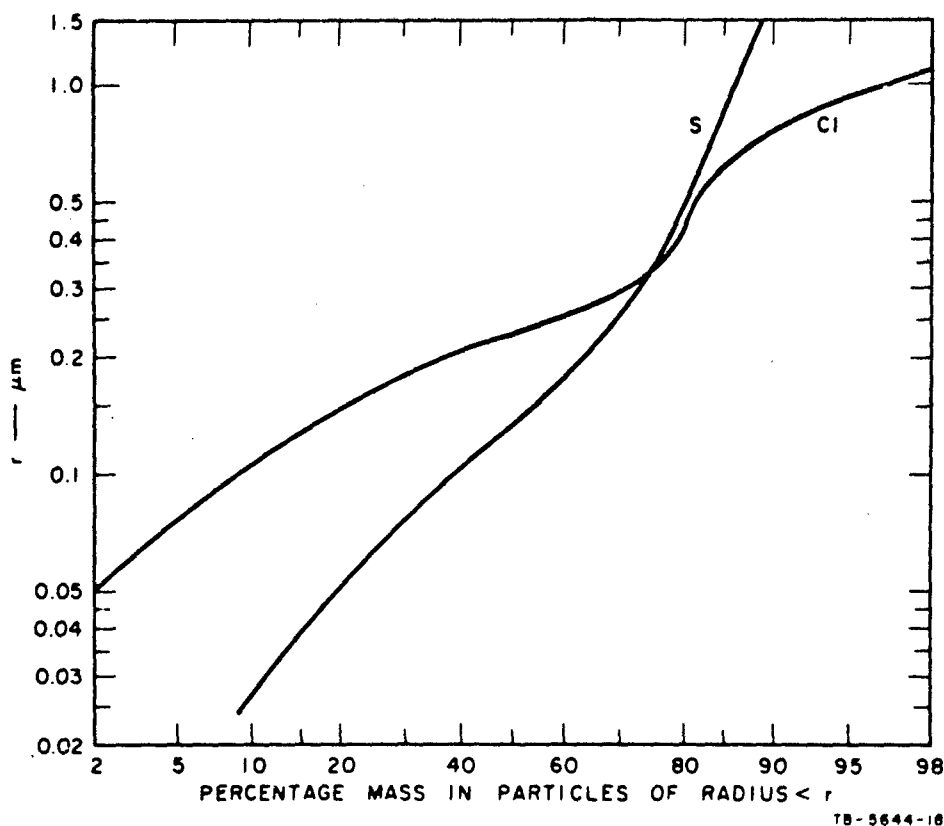


FIG. 21 SULFUR AND CHLORIDE AEROSOL SIZE DISTRIBUTIONS, CRATER LAKE, SAMPLE 1

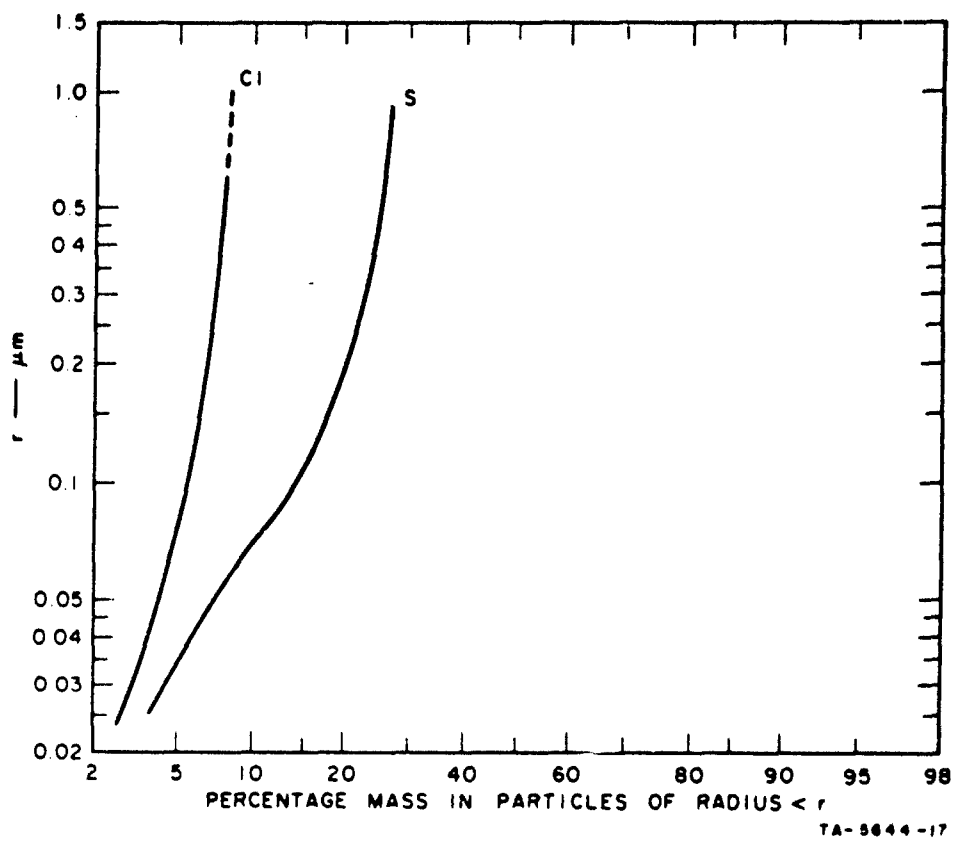
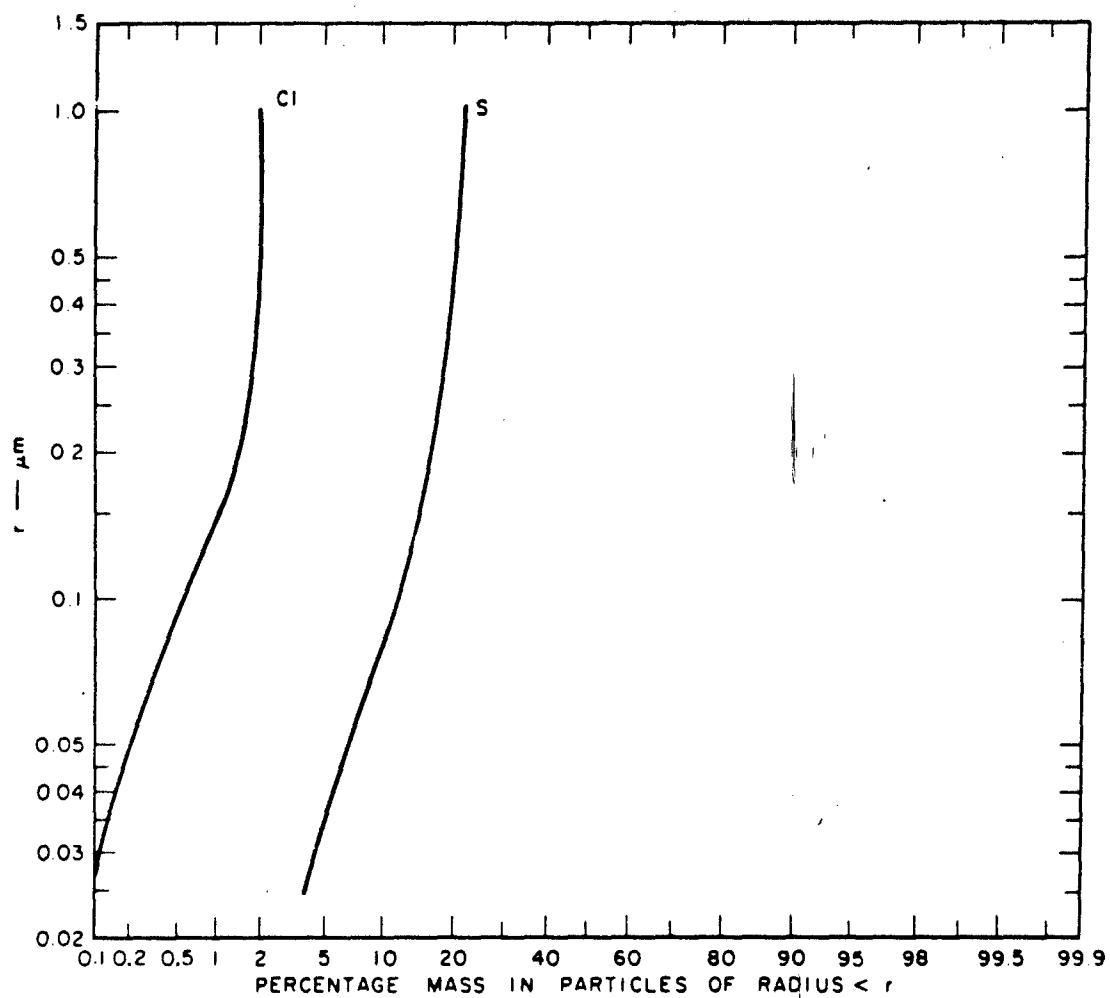


FIG. 22 SULFUR AND CHLORIDE AEROSOL SIZE DISTRIBUTIONS, CAPE BLANCO, SAMPLE 2



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FIG. 23 SULFUR AND CHLORIDE AEROSOL SIZE DISTRIBUTIONS,  
CAPE BLANCO, SAMPLE 3

Table V  
COMPARISON OF THE SIZE DISTRIBUTIONS OF SULFUR

Radius of Sulfur Particles (Radius Interval), $\mu\text{m}$	Sample 1 Crater Lake		Sample 2 Cape Blanco		Sample 3 Cape Blanco	
	%	Absolute Concen- tration, $\mu\text{g}/\text{m}^3$ STP	%	Absolute Concen- tration, $\mu\text{g}/\text{m}^3$ STP	%	Absolute Concen- tration, $\mu\text{g}/\text{m}^3$ STP
$\leq 0.025$ (0.025-0.05)	9	0.041 (0.048)	4	0.043 (0.033)	4	0.027 (0.021)
$\leq 0.05$ (0.05-0.10)	20	0.090 ( <u>0.086</u> )	7	0.076 (0.075)	7	0.048 (0.028)
$\leq 0.10$ (0.10-0.25)	39	0.176 (0.034)	14	0.151 ( <u>0.087</u> )	11	0.076 ( <u>0.042</u> )
$\leq 0.25$ (0.25-0.5)	69	0.310 (0.040)	22	0.238 (0.032)	17	0.118 (0.020)
$\leq 0.5$ (0.5-1.0)	80	0.360 (0.026)	25	0.270 (0.022)	20	0.138 (0.014)
$\leq 1.0$	86	0.386	27	0.292	22	0.152
$\geq 1.0$		(0.064)		(0.788)		(0.538)
Total	100	0.450	100	1.080	100	0.690

Values in parentheses give concentrations for the corresponding radius intervals. Maximum interval concentrations are underlined.

Table V shows that the absolute concentrations for radii less than  $1.0 \mu\text{m}$  for all three samples do not differ by more than a factor of 2 to 3. Considering the differences in air masses and sampling locations, this means a rather uniform distribution of sulfur in the smaller particle size range throughout air masses of predominantly Pacific origin. The fact that concentrations in the various radius intervals are generally higher at Crater Lake suggests that the source of this sulfate aerosol is at these altitudes while the sink area is at the sea surface, in accord with our suggestion of predominant continental origin of these aerosols. However, this may be reading too much into these two values. At the upper end of the size spectrum, for sizes larger than  $1 \mu\text{m}$  radius,

there is a considerable shift to high concentrations for the Cape Blanco data: 0.064 for Crater Lake as compared to 0.788 and 0.538  $\mu\text{g}/\text{m}^3$  for both Cape Blanco samples. There is little doubt that this difference is due to the sea spray sulfate. It is known that the sea spray component of atmospheric aerosols is, mass-wise, almost completely concentrated in the particle range  $r > 1 \mu\text{m}$ , as is demonstrated by Woodcock's data (Junge, 1963, Fig. 24).

The sea salt origin of the sulfur in the giant particles ( $>1 \mu\text{m}$ ) is indicated by a comparison with the chloride data discussed later. Using the information in Table X we obtain concentrations for particles larger than  $1 \mu\text{m}$  radius given in Table VI. The ratio  $\text{Cl}/\text{SO}_4$  in sea water is 7.3, which is in reasonable agreement with our values of 8.7 and 9.4. This comparison shows that there cannot be much fractionation of  $\text{SO}_4$  during the formation of the sea spray aerosols and gives at the same time some idea of the quality of the data.

Table VI  
CHLORIDE AND SULFATE PARTICLES  $>1 \mu\text{m}$  AT CAPE BLANCO

	Sample 2	Sample 3
Sulfur conc., $\mu\text{g}/\text{m}^3$	0.79	0.69
Sulfate conc., $\mu\text{g}/\text{m}^3$	3.2	2.1
Chloride conc., $\mu\text{g}/\text{m}^3$	30.0	18.2
Ratio $\text{Cl}/\text{SO}_4$	9.4	8.7

The rather uniform sulfur distribution for particles smaller than about  $0.5 \mu\text{m}$  seems to represent the low tropospheric background aerosol for Pacific air masses. These are the first though still not sufficiently representative data of their kind.

In all three samples there is an indication that the maximum sulfate density is around  $0.1 \mu\text{m}$  radius. This is in agreement with theoretical results on the chemical composition of tropospheric equilibrium aerosols which suggest that most of the sulfate in such aerosols comes from the oxidation of background  $\text{SO}_2$  in the troposphere and must be expected in the size interval around  $0.1 \mu\text{m}$  radius (Junge and Abel, 1965).

In Fig. 24 we have plotted the mass distribution of  $\text{SO}_4$  according to Table V. As an example of the method of conversion to this type of plot: we took the value of  $0.086 \mu\text{g}/\text{m}^3$  for the particle range  $r = 0.05$  to  $0.10 \mu\text{m}$ , multiplied it by 3 to convert it to sulfate, because sulfur will be present in this form, and divided this value by  $\Delta \log r = 0.3$ , obtaining

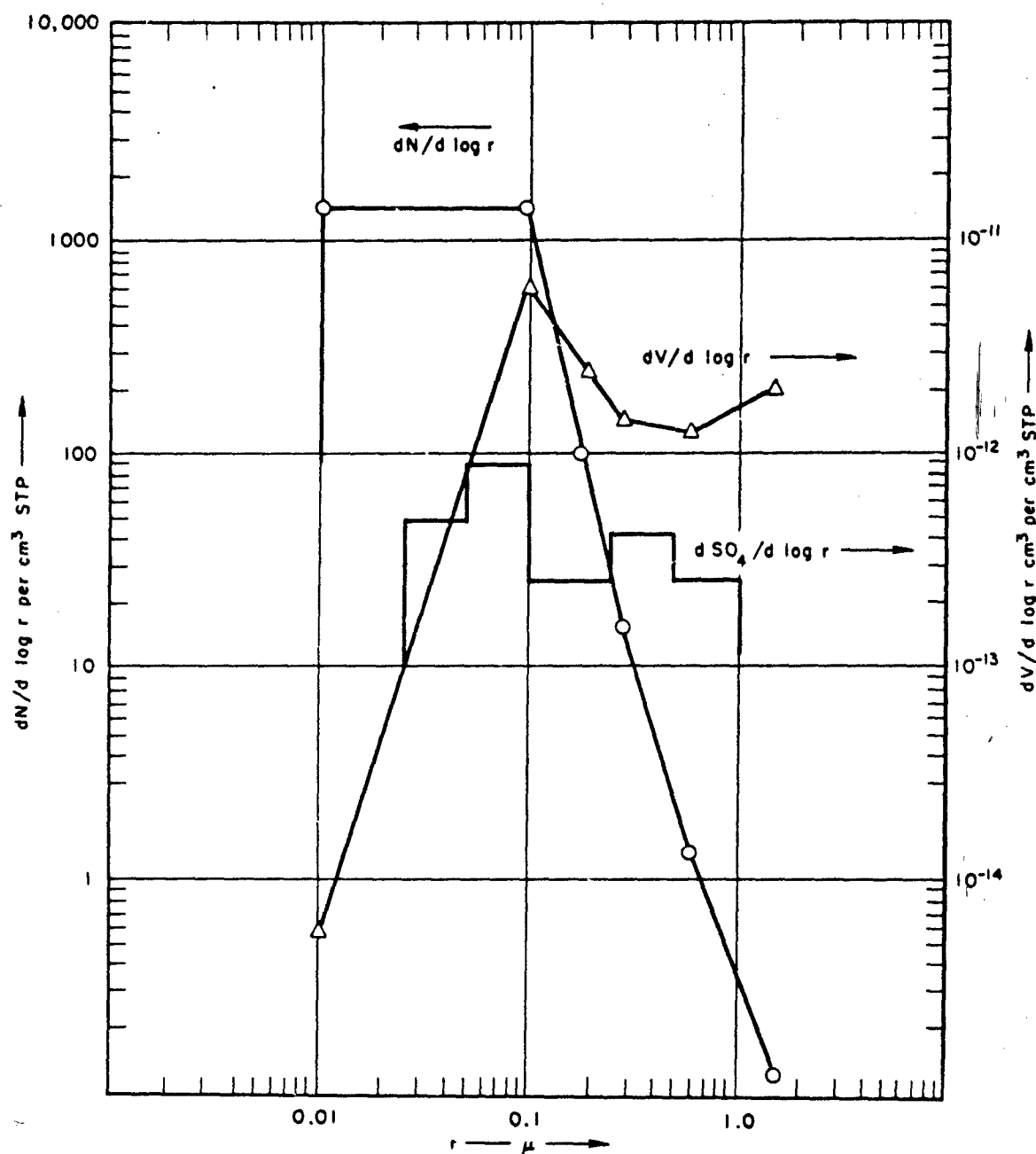
$$d\text{SO}_4/d \log r = \frac{3 \times 0.086}{0.3} \times 10^{-12} = 0.86 \times 10^{-12} \text{ g}/\text{cm}^3$$

If we assume a density of one for the natural aerosols, considering some water content, we can plot these values on the  $dV/d \log r$  scale and compare them with those of the size distribution (Fig. 24). Except for the lower end of the size distribution, where difficulties arise from our lack of knowledge about the actual distribution of the Aitken particles, we see that on the average about 25% of the aerosol volume or mass can be represented by sulfate. This indicates the existence of other constituents, most likely organic material as Goetz has suggested several times (e.g., Goetz *et al.*, 1961). Of course, one should refrain from putting too much weight on the value of 25%, because the data are hardly representative enough for average conditions. The value seems to be of the right order, however, and the quality of the data is generally quite satisfactory, as suggested by the fact that the distribution of  $\text{SO}_4$  runs roughly parallel to the mass distribution curve of the size distribution curve of the size distribution for  $r \geq 0.1 \mu\text{m}$ .

#### C. Chloride Field Sampling Data

Most of what was said about obtaining size distributions of sulfur applies also to chloride. Generally the background of chloride on the linings and filters was higher, and at Crater Lake the concentrations were in all size ranges lower than for sulfur, so that for this site the net values are less reliable than for sulfur.

For Cape Blanco the chloride concentrations are higher in all size ranges, so that the net chloride values are probably as accurate or perhaps better than the sulfur data.



78-5644-21

FIG. 24 COMPARISON OF THE VOLUME DISTRIBUTION  $dV/d \log r$  FOR CRATER LAKE, CALCULATED FROM THE NUMBER DISTRIBUTION  $dN/d \log r$  AND THE MASS DISTRIBUTION OF SULFATE  $dSO_4/d \log r$  FOR CRATER LAKE SAMPLE 1

The analysis of the chloride samples gave the following results:

Sample 1: Crater Lake, October 28 to November 2, 20 hours  
(Table VII). A.S. sample volume, 19.6 m<sup>3</sup>.

Total filter sample volume, 44 m<sup>3</sup>.

Total Cl concentration of A.S. and clean-up filter,  
0.06 µg Cl/m<sup>3</sup> STP.

Total Cl concentration of total filter, 0.04 µg Cl/m<sup>3</sup> STP.

Table VII  
CHLORIDE DATA, CRATER LAKE, SAMPLE 1

Section of A.S. Lining	Cut-off Diameter of Section Cuts, µm	Net Cl Values of Sections after Subtraction of Blanks, µg	Cumulative Net Cl Values, µg	Cumulative %
a		0.24	1.11	100.0
b	1.70	0.24	0.87	78.5
c	0.82	0.35	0.63	56.8
d	0.84	0.21	0.28	25.2
Clean-up filter		0.07	0.07	6.3
Total		1.11	1.11	100.0

In view of the generally low concentrations and the background levels, the agreement between the two values is considered satisfactory, and 0.06 was accepted as the final value.

Sample 2: Cape Blanco, November 4 to 6, 20 hours (Table VIII).  
A.S. sample volume, 10.5 m<sup>3</sup>.

Total filter sample volume, 26.1 m<sup>3</sup>.

Gas filter sample volume, 20.2 m<sup>3</sup>.

Total Cl concentration of A.S. and clean-up filter,  
5.1 µg Cl/m<sup>3</sup> STP.

Total Cl concentration of total filter, 19.5 µg  
Cl/m<sup>3</sup> STP.

Total Cl concentration of gas filter, 32.4 µg  
Cl/m<sup>3</sup> STP.



Table VIII  
CHLORIDE DATA, CAPE BLANCO, SAMPLE 2

Section of A.S. Lining	Cut-off Diameter of Section Cuts, $\mu\text{m}$	Net Cl Values of Sections after Subtraction of Blanks, $\mu\text{g}$	Cumulative Net Cl Values, $\mu\text{g}$	Cumulative
a		315.0*	340.0	100.0
b	1.70	1.9	24.7	7.2
c	0.82	2.9	22.8	6.7
d	0.48	3.9	19.9	5.8
Clean-up filter		16.0	16.0	4.7
Total		340.0	340.0	100.0

\* Corrected give a total concentration of  $32.4 \mu\text{g Cl/m}^3$  STP.

The value for a was increased to give the same total concentration as the gas filter sample. This is the same procedure adopted for the sulfur values.

Sample 3: Cape Blanco, November 8 to 9, 20 hours (Table IX).  
A.S. sample volume,  $10.4 \text{ m}^3$ .

Total filter sample volume,  $26.2 \text{ m}^3$ .

Gas filter sample volume,  $14.4 \text{ m}^3$ .

Total Cl concentration of A.S. and clean-up filter,  
 $2.2 \mu\text{g/m}^3$  STP.

Total Cl concentration of total filter,  $13.2 \mu\text{g/m}^3$  STP.

Total Cl concentration of gas filter,  $18.6 \mu\text{g/m}^3$  STP.

As with sulfur, we can compare the ratios of the various concentrations for samples 2 and 3:

Sample 2:  $5.1 : 19.5 : 32.4 = 1 : 3.8 : 6.4$

Sample 3:  $2.2 : 13.2 : 18.6 = 1 : 5.9 : 8.4$

Table IX  
CHLORIDE DATA, CAPE BLANCO, SAMPLE 3

Section of A.S. Lining	Cut-off Diameter of Section Cuts, $\mu\text{m}$	Net Cl Values of Sections after Subtraction of Blanks, $\mu\text{g Cl}$	Cumulative Net Cl Values, $\mu\text{g}$	Cumulative %
a		191.3*	194.9	100.0
b	1.70	0.6	3.6	1.9
c	0.82	0.9	3.0	1.5
d	0.48	1.3	2.1	1.1
Clean-up filter		0.8	0.8	0.4
Total		194.9	194.9	100.0

\* Corrected to give a total concentration of  $18.8 \mu\text{g Cl}/\text{m}^3$  STP.

The agreement between the two samples is not as good as with sulfur, but one should consider in this connection the great variability of the sea salt component near the ocean. This is also partly reflected in the difference of the total concentrations.

Another discrepancy which is not so easy to explain is the relatively high clean-up filter value for sample 2 as compared with sample 3. This would indicate, if it is valid, a very high concentration of very small particles, i.e., less than  $0.13 \mu\text{m}$  radius; there is no reason for such a high concentration. All data were carefully rechecked to see if any analytical error might be involved, but none was found. Although we feel that perhaps an undetected contamination of the clean-up filter might be involved here, we have no way of checking on it and have to accept the value as it stands. A lower clean-up value would bring the ratios of the total concentrations into better agreement with sample 3.

#### D. Discussion of Chloride Data

Figures 21 to 23 show the relative cumulative chloride distributions. From these plots we obtain the data in Table X for comparison of the three tests.

Table X  
COMPARISON OF THE SIZE DISTRIBUTIONS OF CHLORIDE

Radius of Cl Particles, $\mu\text{m}$	Sample 1, Crater Lake		Sample 2, Cape Blanco		Sample 3, Cape Blanco	
	%	Absolute Concentration, $\mu\text{g}/\text{m}^3$ STP	%	Absolute Concentration, $\mu\text{g}/\text{m}^3$ STP	%	Absolute Concentration, $\mu\text{g}/\text{m}^3$ STP
$\leq 0.025$	--	--	2.8	0.91	--	--
$\leq 0.05$	2	0.0012	4.2	1.36	--	--
$\leq 0.10$	9	0.0054	5.5	1.78	0.2	0.037
$\leq 0.25$	59	0.0350	6.8	2.2	1.7	0.316
$\leq 0.50$	81	0.0485	7.5	2.4	1.9	0.354
$\leq 1.00$	97	0.0581	8.0	2.6	2.0	0.372
Total	100	0.0600	100	32.4	100	18.6

The over-all weather during the Crater Lake period was characterized by a high pressure extending from the Pacific to our area; low pressure systems moved eastward at higher latitudes with their frontal systems touching our area. All trajectories of the air masses at 700 mb from October 28 to November 2 show advection of Pacific air masses from the southwest sector. Winds at this level at Medford, Oregon, which is located approximately between Crater Lake and Cape Blanco and is thus fairly representative of our sampling areas, confirm this. Below the 850 mb level the winds at Medford were light and variable. This fact, plus the configuration of the surface weather map, makes it doubtful whether there was much advection from the ocean at lower levels, although such a situation is suggested by the general movement of the frontal systems.

If we compare the Crater Lake data in Tables V and X, we see that the relative distribution of chloride is similar to that of sulfur. The chloride concentrations are, however, less than those of sulfur by a factor of about 8 and less than those of sulfate by a factor of about 25. This indicates that the aerosols below 1  $\mu\text{m}$  radius at this level have quite a different composition from sea spray even for air masses

of definite maritime origin. This supports the idea that these aerosols are aged continental aerosols modified by various meteorological processes. This concept is of some importance for cloud physics, since it is this size range which supplies most of the particles used in cloud droplet formation.

Particularly puzzling is the very low total chloride concentration of the Crater Lake sample of only  $0.06 \mu\text{g}/\text{m}^3$  STP, a value which was confirmed by the total filter sample. Since the only real analytical problem in our case was contamination, which always tends to increase the net values, we have to accept this low concentration as a representative value for our sampling period. Even if there was no advection from the ocean below about 800 mb, this low concentration is somewhat hard to understand, because one would expect that vertical mixing over the ocean would transport part of the sea spray aerosol accumulated in the surface layers to the altitude of Crater Lake. It should be mentioned that all vertical profiles of sea spray particles which we have found in the literature show a decrease in concentration between 1 and 2 kilometers by one or more orders of magnitude (see, e.g., Junge, 1963, Fig. 36). All these profiles were obtained by Woodcock in Florida, Hawaii, and Australia, i.e., in areas which frequently show strong subsidence inversions at this altitude, so that the decrease in sea spray aerosols is to be expected. It is doubtful if this explanation can also be applied to our case. It is very unfortunate that no vertical profiles are available for the latitudes of the westerlies to which our data should be comparable.

The low total chloride concentrations are even harder to understand if there was advection from the ocean below 800 mb during the period of the Crater Lake sample. If we assume in these air masses surface layer concentrations similar to those of our Cape Blanco samples, we should expect higher chloride concentration at the Crater Lake level. There was practically no rain or washout in our coastal areas during the period in question, and vertical convection over the mountainous region of southern Oregon should have transported at least a small fraction of the sea spray upward. One should consider that the total

chloride concentrations in the Cape Blanco samples are higher by more than one order of magnitude, so that even small fractions of the surface layer aerosols should be detected at the Crater Lake level. On the other hand, in case of advection, it is understandable that the sulfate concentrations below 1  $\mu\text{m}$  radius are almost the same for Crater Lake and Cape Blanco, since the air masses in both levels would be of similar, i.e. maritime, origin. In case of no advection from the ocean, this would not be easy to understand.

The chloride distributions at Cape Blanco are quite different from those of Crater Lake. In sample 3 more than 98% of the chloride is concentrated in particles larger than 1  $\mu\text{m}$  radius. This value agrees well with earlier data obtained in Hawaii (see Junge, 1963, Fig. 24) where almost the same percentage was found. For sample 2 this value is 92%, but we have already mentioned our doubts about the reliability of this distribution. These chloride analyses strongly support our suggestion that the difference in Fig. 19 between the size distributions of Crater Lake without subsidence and Cape Blanco are due to the sea spray component. In the discussion of the sulfur data we showed that the high sulfate concentrations found above 1  $\mu\text{m}$  radius are quite consistent with the sea water composition. However, for the smaller particles below 1  $\mu\text{m}$  radius things are more complex. Sample 3 for chloride shows concentrations at Cape Blanco to be higher by a factor of about 10 than at Crater Lake even for particles as small as 0.1  $\mu\text{m}$ . The difference in concentration is even more pronounced in sample 2. These high chloride concentrations seem to indicate the presence of a sea spray chloride component in the 0.1  $\mu\text{m}$  radius range which is mass-wise of the same order as the sulfur component. As a consequence of vertical mixing over the ocean and of the lower efficiencies in washout and rainout in the particle size range around 0.1  $\mu\text{m}$  radius, one would expect a rather uniform chloride concentration in maritime air masses in this size range. Apparently any aerosols formed at the sea surface have little chance to penetrate to higher layers over the oceans. Unfortunately, our data are too few to draw any general conclusions, but it seems to us that these results still indicate a considerable lack of basic knowledge in the field of tropospheric aerosols.

## 1. Other West Coast Chemical Aerosol Studies

One of the primary purposes of the studies described here was to help fill the gaps in existing knowledge of the chemical composition and size distribution of natural aerosols. For this reason we would not expect to find a large amount of data to compare with those collected on this project. The available data are primarily total mass concentration values rather than detailed aerosol studies. In this regard, Holzworth (1958), Lodge et al. (1960), Duce et al. (1965), and the U.S. Public Health Service (1958), among others have made measurements of chloride or sulfate aerosol concentrations in nonurban areas along the West Coast of the United States and in Hawaii. Size distribution studies of chloride and sulfate aerosols have been made in West Coast urban areas by Ludwig et al. (1966), and Duce's data include some estimates of size distributions of halide particles in marine air in Hawaii.

These data are summarized in Table XI. With the exception of the U.S. size distribution studies of Ludwig et al. (1966), we have not included any data from locations which are apt to be strongly affected by urban pollution sources. In addition to the average sulfate and chloride concentration, we have included averages of the concentrations of total suspended matter where available.

In general the  $\text{SO}_4$  values of Holzworth are somewhat higher than the other data, most of which suggest a background of about  $5 \mu\text{g SO}_4/\text{m}^3$  or  $1.7 \mu\text{g}/\text{m}^3$  sulfur. One is tempted to interpret this as the natural background, but our data from Cape Blanco indicate levels lower by a factor of 2 to 3.

The published chloride values scatter considerably because of local conditions of surf, etc. In addition there is a rapid decrease of concentration inland, and it is hard to compare these data in a meaningful way with our values.

The sulfate size distributions of Ludwig et al. (1966) indicate that the urban sulfate sizes are about the same as those observed at Crater Lake, but substantially smaller than those observed at Cape Blanco. Urban chloride measurements made by these same investigators indicate

Table XI  
STUDIES OF SULFATE AND CHLORIDE AEROSOLS IN WEST COAST AND PACIFIC AREAS

LOCATION	TOTAL SUSPENDED MATTER $\mu\text{g m}^{-3}$	$\text{SO}_4$ $\mu\text{g m}^{-3}$	Cl $\mu\text{g m}^{-3}$	REFERENCE	REMARKS	SITE DESCRIPTION
Pt. Woronzof, Cook Inlet, Alaska	37	4.4	0.3	U.S. Public Health Service, 1958	63 samples total particulate, 12 samples Cl and $\text{SO}_4$	Forest, 190 ft elev., Arctic Health Res. Center; filters
Crescent City, Calif.	358 184	19.5 14.8* 13.5 9.6*	34 28	Holzworth, 1959 Ibid.	Winds from land, 23 samples Winds from ocean, 24 samples	Coast Guard Light Station, 45 ft elev., surf influence, Aug. 1956-Jan. 1957; filters
S.E. Farallon Island, Calif.	95 184	12.6 11.3* 13.6 3.8*	9.1 70.6	Ibid. Ibid.	Winds from land, 27 samples Winds from ocean, 72 samples	Coast Guard Light Station, near sea level, 30 mi west of Golden Gate, strong surf influence, Jan.-Dec. 1956; filters
Pt. Piedras Blancas, Calif.	578	38.7 21.7*	122	Ibid.	Trajectory along coast, 29 samples	Coast Guard Light Station half way between Los Angeles and San Francisco, 35 ft elev., May 1956-Jan. 1957; filters
San Nicolas Island, Calif.	291	18.6 9.9*	63	Ibid.	Minimum coastal trajectory, 28 samples	Island airfield 70 mi west of Los Angeles, 500 ft elev., May 1956-Jan. 1957; filters
Los Angeles, Calif.	64	8.4	2.0	Ibid.	Mostly ocean trajectory, 9 samples	Downtown Los Angeles; A.S. and filters, some cascade impactor
Menlo Park, Calif.	--	12.1	3.9	Ludwig <i>et al.</i> , 1966	Approx. $0.4 \mu\text{m MMD}$ sulfate Approx. $0.3 \mu\text{m MMD}$ chloride 51 sulfate samples, § 22 chloride samples §	Stanford Research Institute; A.S. and filters
Kings Landing, Hawaii	--	4.6	0.8	Ibid.	Approx. $0.3 \mu\text{m MMD}$ sulfate 21 $\text{SO}_4$ samples; § 12 Cl samples §	50 yd from breaking surf; cascade impactor
Hilo, Hawaii	--	--	90 <sup>Δ</sup>	Duce <i>et al.</i> , 1965 Ibid.	Average of 3 samples 31 $\mu\text{g m}^{-3}$ ~ 7 $\mu\text{m}$ 83 $\mu\text{g m}^{-3}$ ~ 2 $\mu\text{m}$ 86 $\mu\text{g m}^{-3}$ ~ 1 $\mu\text{m}$ 1 sample 0.3 $\mu\text{g m}^{-3}$ ~ 7 $\mu\text{m}$ 2.0 $\mu\text{g m}^{-3}$ ~ 2 $\mu\text{m}$ 2.3 $\mu\text{g m}^{-3}$ ~ 1 $\mu\text{m}$	National Guard Base, sea level 1/2 mi from shore; cascade impactor





much the same situation as with sulfate: Sizes are comparable to those found at Crater Lake, but substantially smaller than the chloride size distributions found at Cape Blanco.

The Hawaiian results of Duce et al. (1965) are not wholly comparable to the measurements presented here, because they did not collect particles smaller than about 0.5  $\mu\text{m}$  with their cascade impactor. However, their data do not contradict our results.

## VI SUMMARY AND DISCUSSION

As a result of our aerosol studies in remote areas of southern Oregon, we have come to a number of interesting conclusions pertaining to general aerosol conditions in the troposphere. It should be pointed out that these conclusions are still tentative in respect to their large-scale or global aspects, because the experimental and observational basis is still much too limited, but even in their present form these conclusions may at least contribute to a clarification of the broad picture of atmospheric aerosol distributions about which we know so little.

Broadly speaking, we can distinguish three types of atmospheric aerosols in Pacific air masses of middle and lower latitudes:

1. Aerosols of the surface marine air.
2. Aerosols of low- to mid-tropospheric layers, i.e., between 2000 and 3000 meters altitude.
3. Aerosols of high tropospheric layers.

The aerosol characteristics of surface marine air differ essentially from the mid-tropospheric aerosol by the addition of the typical sea spray component. This sea spray component has, so far as we know, a mode in the size distribution around  $0.5\ \mu\text{m}$  radius and a sulfur to chloride ratio of about 0.04, close to that of sea water. This indicates little or no fractionation of at least these two constituents during aerosol generation by the bubble bursting process. Our present findings in terms of size distribution and chemical composition are well in accord with earlier data from other investigators about the sea salt aerosol (see, e.g. Junge, 1963).

In addition, our data strongly indicate that no significant amounts of sea spray aerosol penetrate to altitudes of 2500 meters, even in Pacific air masses of apparently long maritime history. Similar results had already been found in areas at lower latitudes where subsidence is

more pronounced and, therefore, where a restriction to shallow layers is understandable. However, these findings are new for air masses within the belt of westerly winds. These results may indicate that it is generally very difficult for large fractions of the sea spray aerosol to penetrate to higher layers because of the high efficiency of rainout processes for these aerosols.

The low- to mid-tropospheric aerosol is characterized by size distributions which can be well approximated by a power law with exponential values of 3 to 4, by sulfur to chloride ratios of about 8, and by the presence of considerable amounts of substances other than sulfate and chloride. These other substances may well be organic matter, as suggested by Goetz et al. (1961). In this mid-tropospheric aerosol the sulfate seems to be primarily concentrated in the size range around  $0.1 \mu\text{m}$  radius. We think that this low- to mid-tropospheric aerosol represents an aged continental aerosol modified, as considered by Junge and Abel (1965), by a variety of meteorological processes during travel around the world. To consider this aerosol to be of marine origin would require a number of very doubtful conditions to prevail. First, there would have to be a very special process of sea surface particle formation quite different from the bubble bursting process. This process would have to produce high-sulfate particles with a S/Cl ratio of 8 instead of the sea spray ratio of 0.047 and at the same time incorporate large amounts of non-sea-salt substances in the particles. These particles, furthermore, would have to be predominantly small particles around  $0.1 \mu\text{m}$  and relatively unaffected by rainout and washout processes as they penetrate to higher atmospheric layers. We do not consider such a complicated process reasonable, and therefore we have concluded that the aerosols we observed in low- and mid-tropospheric air masses were not of marine origin.

The aerosols of the high troposphere, which are associated with subsidence, have much lower concentrations than are characteristic of lower tropospheric aerosols. Also, the power law size distributions of the high tropospheric aerosols have much smaller exponential values than

is the case for low- to mid-tropospheric distributions. These characteristics are considered to be representative of aerosol conditions in the high troposphere. Because of low concentrations and limited sampling opportunities, we were not able to obtain information on the chemical composition of the high tropospheric aerosol. Chemical composition would be of interest but will be difficult to determine. The fact that our size distribution agrees nicely with corresponding data from 3000 meters in Hawaii indicates that this aerosol is rather uniform and wide spread in the upper troposphere. It is also likely, all things considered, that it represents a further stage in the reduction and aging of continental aerosols. Because of the nature of the general circulation of our atmosphere, it is possible that this aerosol is the most common one in the troposphere and represents a rather uniform background condition.

Of all the findings of interest which are pointed out in the text of this report, we believe that the most significant is the conclusion that the sea spray aerosol is restricted to rather shallow surface layers even in midlatitude air masses of long maritime history, and that the tropospheric aerosols on which the sea spray aerosol is superimposed is of distinctly different character. Most likely the background aerosol is of a continental origin in which only a negligible fraction can be attributed to processes active at the sea surface.

**Appendix A**  
**SAMPLING EQUIPMENT AND METHODS**

Appendix A

SAMPLING EQUIPMENT AND METHODS

A. Aerosol Spectrometer

1. Operating Principles

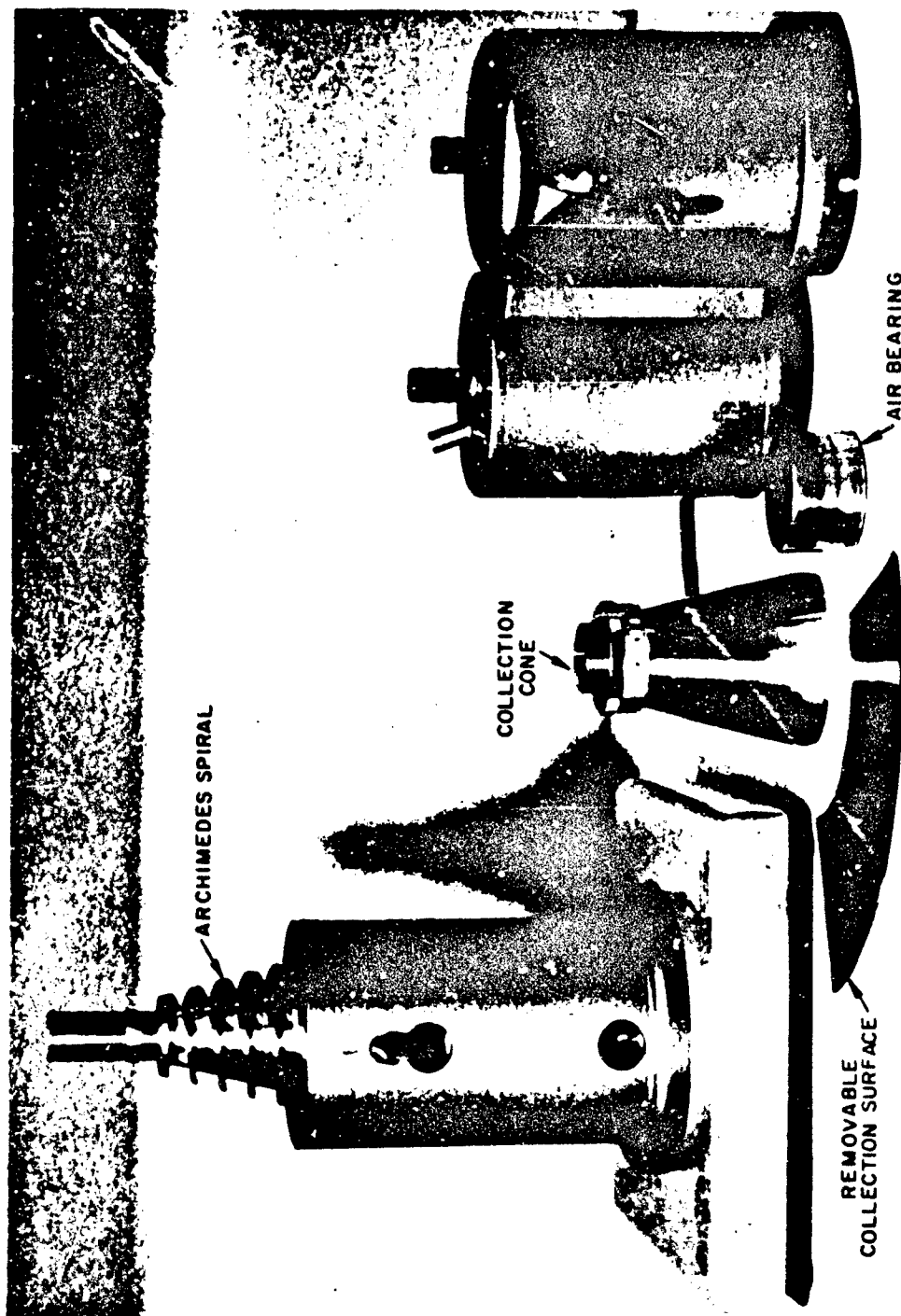
The Goetz Aerosol Spectrometer (A.S.) consists of three separate units: a centrifuge which collects and separates by size the air-borne particulate material, a cooling system, and a console which controls the rate of rotation of the centrifuge and monitors the temperature differential between the ambient air and the air passing through the instrument. A refrigerated circulating coolant is used to maintain the A.S. operating temperature at or near ambient.

A centrifuge unit is shown partially disassembled in Fig. A-1. The rotor of the instrument has two helical channels through which the air passes from the top toward the bottom. An exact-fitting conical cup is placed over the outside of the rotor channels during operation. The interior surface of the cup is lined with a removable collection surface. The air is propelled through the channels by their helical configuration and the rotation of the rotor. For any given rate of rotation, the air flow is governed by the restricting orifices at the exits of the two channels. Details of construction and operation can be obtained from the instructions supplied with the instrument\* or from Goetz et al. (1960).

For the determination of cumulative mass distributions it is necessary to determine the amount of material which passes uncollected through the A.S. This material is collected on a filter attached to the outlet of the A.S. A pump is necessary to pull the air through this "cleanup" filter. The pumping rate is adjusted so that there is no pressure difference between the A.S. exit and the atmosphere.

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\* Zimney Corporation, 160 Taylor St., Monrovia, California.



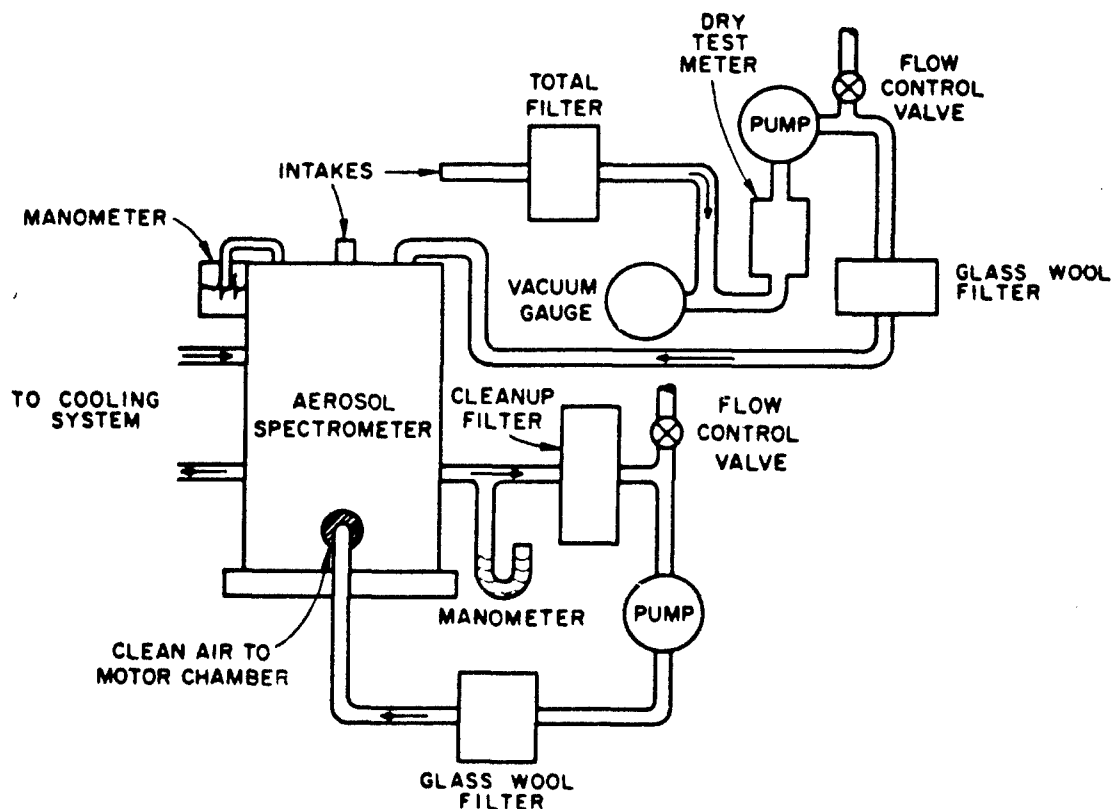
(Courtesy Zimney Corp., Monrovia, Calif.)

RP-4211-9

FIG. A-1 AEROSOL SPECTROMETER PARTIALLY DISASSEMBLED SHOWING MAJOR COMPONENT PARTS

Filtered air is circulated around the bearings of the A.S. rotor to prevent entrainment of contaminated air into the system at points where it can cause errors in the analysis. Also, this filtered air introduces a slight super-pressure in the chambers surrounding the bearings, and prevents loss of sample through the bearings. Figure A-2 shows the arrangements of the equipment as it was used with the recirculated filtered air.

A separate filter, labeled "total filter" in Fig. A-2, was used to collect aerosol samples independently of the aerosol spectrometer. The samples from this filter, referred to as "total" or "filter" samples, provide a check on the general performance of the A.S. and information on ambient concentrations.



RA-4740-2

FIG. A-2 SCHEMATIC DIAGRAM OF SAMPLING SYSTEM



## 2. Size Distribution Determinations

From the description of the A.S., it is evident that the centrifugal action of the spinning cone causes particles in the air to be deposited on the collection surface. Aerosol particles of larger size and mass are precipitated faster than smaller particles. For particles of a given size and for a specific set of operating conditions, there is a maximum distance down the channels to which such particles may penetrate. It is also evident that the forces to which the particles are subjected are different at different parts of the channel, and it is therefore better not to apply to the A.S. the conventional methods of particle size analysis used for settling chambers.

It would be expected from the Stokes equation for settling velocity of a particle that the rate of deposition at any point in the channel is proportional to the radial acceleration  $G(L)$  at the point  $L$  and to the square of the diameter of the particle. Similarly, if the Cunningham correction is applied, the deposition rate would be expected to be proportional to the product of the radial acceleration and a term which is the sum of the square of the diameter and a constant times the diameter. From this we infer that the deposition rate would be expected to be proportional to the radial acceleration times some function of the diameter,  $f(D)$ . This, of course, assumes the particles to differ only in size, not in density. Equations can be written for the fraction  $F(D)$  of the total mass of particles of diameter  $D$  which are deposited in the A.S. before reaching some fixed distance  $L_D$  down the channel. The equation for  $F(D_G)$  is

$$F(D_G) = kf(D_G) \int_0^{L_D} G(L) dL = 1 \quad (1)$$

where  $k$  is a constant and  $D_G$  is the minimum diameter of particles which are totally deposited within the distance  $L_D$  down the channel. The

fraction deposited equals unity because of the defined relation of  $D_G$  to  $L_D$ . For some diameter  $D$ , smaller than  $D_G$ ,

$$F(D) = kf(D) \int_0^{L_D} G(L) dL \quad (2)$$

Dividing Eq. (2) by Eq. (1) gives

$$F(D) = \frac{f(D)}{f(D_G)} \quad (3)$$

Thus the total mass of materials,  $M'$ , deposited prior to  $L_D$  is given by

$$M'(D_G) = \int_0^{D_G} \frac{f(D)}{f(D_G)} m(D) dD + \int_{D_G}^{\infty} m(D) dD \quad (4)$$

where  $m(D)$  is the mass of the sampled particulate material of diameter  $D$  per unit interval of diameter.

The first term on the right-hand side of Eq. (4) gives the mass of the particles deposited before  $L_D$  with diameters smaller than  $D_G$ . All the particles larger than  $D_G$  will have been deposited; their mass is given by the second term on the right-hand side of Eq. (4).

The total mass of the sampled material,  $M_T$ , is given by

$$M_T = \int_0^{\infty} m(D) dD \quad (5)$$

Thus, the mass of material,  $M$ , deposited in the system (including cleanup filter) beyond  $L_D$  is given by

$$\begin{aligned} M(D_G) &= M_T - M'(D_G) = \int_0^{\infty} m(D) dD - \int_{D_G}^{\infty} m(D) dD - \int_0^{D_G} \frac{f(D)}{f(D_G)} m(D) dD \\ &= \int_0^{D_G} \left[ 1 - \frac{f(D)}{f(D_G)} \right] m(D) dD \end{aligned} \quad (6)$$

If the integrand in Eq. (6) is continuous and has continuous derivatives, Leibnitz's rule can be used to find the derivatives of  $M(D_G)$  with respect to  $D_G$ . Since  $f(D)$  meets these conditions for any reasonable case such as Stokes or Stokes-Cunningham settling, and since the size distribution of particles,  $m(D)$ , in natural aerosols is not likely to be mathematically discontinuous, the derivatives can be taken:

$$\frac{dM}{dD_G} = \int_0^{D_G} \frac{m(D)f(D)}{f^2(D_G)} \frac{d}{dD_G} f(D_G) dD \quad (7)$$

and

$$\frac{d^2 M}{dD_G^2} = \frac{m(D_G)}{f(D_G)} \frac{d}{dD_G} f(D_G) + \left[ \frac{\frac{d^2}{dD_G^2} f(D_G)}{\frac{d}{dD_G} f(D_G)} - \frac{2}{f(D_G)} \frac{d}{dD_G} \right] f(D_G) \frac{dM}{dD_G} \quad (8)$$

Solving for  $m(D_G)$  gives

$$m(D_G) = 2 \frac{dM}{dD_G} - \frac{\frac{d^2}{dD_G^2} f(D_G)}{\left[ \frac{d}{dD_G} f(D_G) \right]^2} f(D_G) \frac{dM}{dD_G} + \frac{f(D_G)}{\frac{d}{dD_G} f(D_G)} \frac{d^2 M}{dD_G^2} \quad (9)$$

The more conventional method of representing the distribution of mass as a function of particle size is as a cumulative size distribution, that is, the percentage of the total mass smaller than some diameter is given as a function of that diameter. The cumulative mass,  $m_c$ , is given by

$$m_c(D_G) = M + \frac{f(D_G)}{\frac{d}{dD_G} f(D_G)} \frac{dM}{dD_G} \quad (10)$$

This equation may be checked by taking its derivative with respect to  $D_G$  which gives Eq. (9).

For the special case of Stokes settling,  $f(D_G)$  equals  $D_G^2$ . Making the appropriate substitutions gives

$$m_c(D_G) = M + \frac{D_G}{2} \frac{dM}{dD_G} \dots \text{for Stokes settling} \quad (10a)$$

For the case where the Cunningham correction is included,  $f(D_G)$  equals  $D_G^2 + 1.72\lambda D_G$ , where  $\lambda$  is the mean free path in air at the ambient conditions, and Eq. (10) becomes

$$m_c(D_G) = M + \frac{D_G}{2} \left( 1 + \frac{1.72\lambda}{2D_G + 1.72\lambda} \right) \frac{dM}{dD_G} \dots \text{for Stokes-Cunningham settling} \quad (10b)$$

If we know the relationship between  $L_D$  and  $D_G$  and if we can measure  $M$ , the mass of material collected in the system beyond  $L_D$  as a function of  $L_D$  (and hence as a function of  $D_G$ ), Eq. (10a) or (10b) allows us to determine the distribution of mass in the aerosol as a function of particle diameter. The calculations can be made in terms of percentages of the total collected mass to yield a size distribution in terms of percentage.

It can be shown that the same cumulative percentage,  $m_c$ , is obtained whether the actual particle diameter or the equivalent unit-density diameter is used. Thus, Eq. (10b) can be used to calculate the equivalent size distribution (in terms of equal Stokes-Cunningham settling velocities of particles of unit density) although the density of the sampled particles may not be known.

### 3. Calibration of the Aerosol Spectrometer

Calibration of the aerosol spectrometer requires that two things be determined: (1) flow rates through the instrument under various operating conditions, and (2) the relationship between  $D_G$  and distance down the channel for each set of operating conditions.

Flow rate and deposition distance calibrations were supplied by the manufacturer and were used for the number size distributions obtained with the A.S. Because of differences in operation of the instrument

used for mass distribution determinations, it was felt that recalibration was necessary. The pumping of filtered air around the upper and lower bearing areas could affect flow rates and deposition patterns. The calibrations made at SRI indicate that this procedure does change the operational characteristics of the A.S., but not by a great amount.

Flow rate calibrations were obtained using a pump, rotameter, and manometer on the A.S. inlet. During a flow test, air was pumped through the rotameter and into the A.S. inlet until the manometer indicated that the pressure in the inlet equaled ambient. In this way the effect of restrictions on the inlet flow were avoided and the air flow through the A.S. could be obtained from the rotameter. The A.S. had an average flow rate at sea level of 8.7 liters/min at an 18,000 rpm rotation rate with 0.06-inch exit orifices, the operating conditions used in the field program.

To determine the maximum distance of penetration for a particle of a given size, monodisperse aerosols of polystyrene latex particles were used. Four particle sizes from 0.34 to 1.30  $\mu$  diameter were available for these calibrations. A De Vilbiss nebulizer was used to generate the aerosol which was sampled by the A.S. After collection, the distance from the inlet to the end of the deposit was measured.

The radial distance, R, from the intersection of the two edges of the A.S. collection surface to the termination of the deposit was measured as shown in Fig. A-3. For this instrument every point on such an arc is the same distance along the channel from the entry port, and this distance can be calculated from the geometry of the instrument. The termination of the deposit was fairly abrupt, but not perfectly so. There was also a slight variation of R from one part of the collection surface to another. Dividers were used to measure a value of R which subjectively averaged the changes of R from one part of the surface to another and the blurring of the termination of the deposit. It was estimated that the error of measurement of termination of the deposit was  $\pm 3$  mm (in R) or less. This corresponds to about 1-1/2 to 2 centimeters in L. Calibrations were carried out with a stainless steel liner. The sea level calibration for

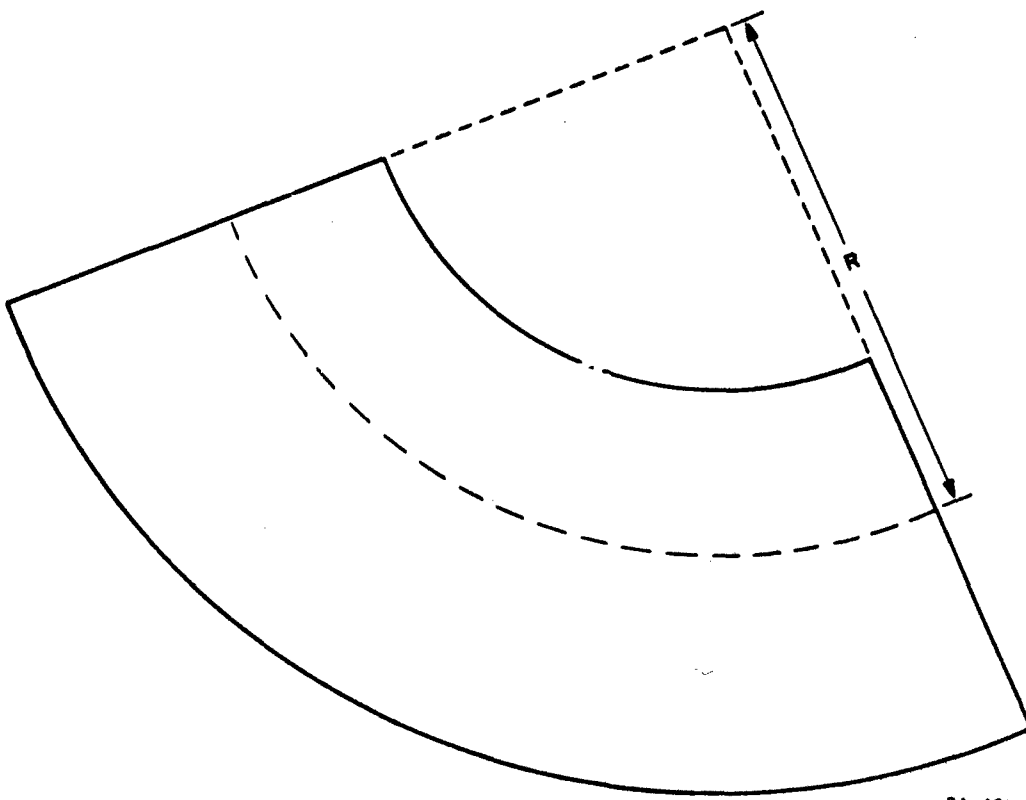


FIG. A-3 AEROSOL SPECTROMETER COLLECTION SURFACE AS MEASURED  
TO DETERMINE DEPOSITION LENGTHS

the 1800 rpm 0.06-inch orifice operating condition is shown in Fig. A-4. Some extrapolation is involved, but the curve is regular, and little error should arise from this source.

#### 4. Pressure Effects on A.S. Calibration

Dr. Alexander Goetz\* was consulted concerning the effect of reduced pressure on the operation of the A.S. He contended that the relationship of  $L_D$  to  $D_G$  would be unchanged by the altitude difference between sea level and Crater Lake. He suggested that differences in flow rate could be determined by attaching a rotameter directly to the A.S. inlet at the two elevations and measuring the flow into the instrument. Dr. Goetz believes that the ratio of these measured flows would be the same as the

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\* Personal communication, 1965.

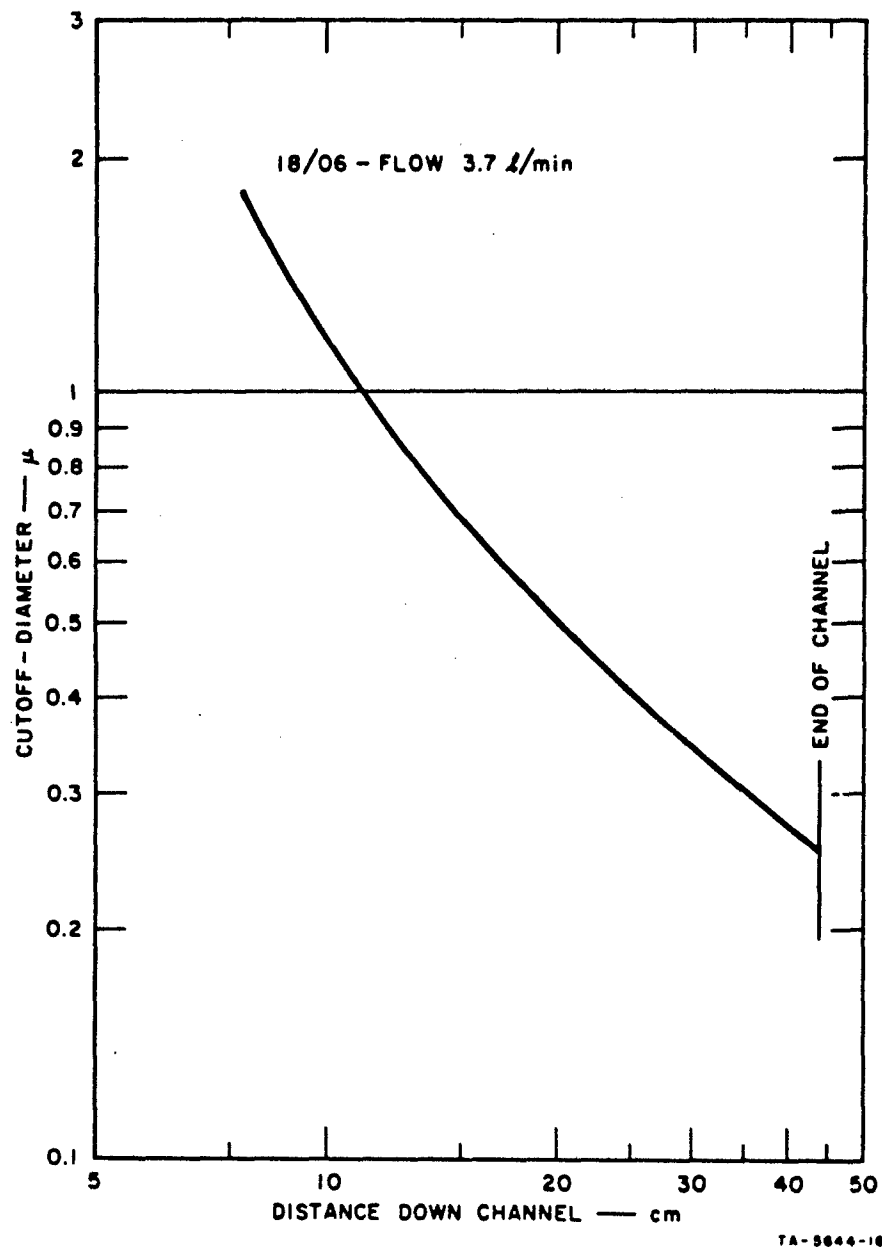


FIG. A-4 CALIBRATION OF AEROSOL SPECTROMETER MODEL 202, SERIAL NO. 150

ratio of the actual flows at the two levels. This was done and the flow rate at Crater Lake for the 18000 rpm, 0.06-inch exit orifice operating conditions was found to be 7.2 standard liter/min.

Concerning the use of the sea-level  $L_D$  vs  $D_G$  calibration for the Crater Lake data, the work of Gerber (1963) is of some interest. He made and compared calibrations at various pressures. Although the particular operating condition used for this program's mass distribution collections is not represented in Gerber's data, some qualitative conclusions can be drawn. Gerber's data indicate that the actual value of  $D_G$  corresponding to a given  $L_D$  at Crater Lake would be somewhat smaller than indicated by the sea level calibration. Information concerning other operating conditions suggests that  $D_G$  would be about 20% less at Crater Lake for the 18000 rpm, 0.06-inch orifice case. The percentage difference would be greatest for the smaller diameter particles.

The change in calibration between sea level and Crater Lake has not been considered in evaluating the data given here, because it is not a large effect compared to other sources of error and because we have no quantitative measure of its magnitude.

##### 5. Filter Efficiency

Gelman Type A glass fiber filter discs (47 mm diameter) were used as cleanup filters for the A.S. and for total particulate sampling (including the prefilters used in our gas sampling attempts). According to the manufacturer (Gelman Instrument Co., 1964), "these filters have been tested to a minimum of 99.8% efficiency for particles in gas streams larger than 0.3  $\mu$ ....The efficiency of these is greater than 98% for particles as small as 0.05  $\mu$  in gas streams." Flow conditions are not specified.

Ludwig et al. (1964) have checked the efficiency of these filters with a General Electric Condensation Nuclei Counter,\* measuring the numbers of nuclei alternately with and without the filter on the intake

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\* Small Particle Detector, Type CN, General Electric Co., Schenectady, New York.



to the instrument. The flow rate was within a factor of 2 of the flow rates used in this problem. These tests indicated efficiencies of the glass fiber filters of greater than 99.9% for condensation nuclei. In the calculations of this report it has been assumed that all particles in the exit air stream have been captured by the filter.

#### 6. Handling of Liners and Filters

The material used for the A.S. liners in the mass size distribution determinations was 0.001-inch-thick stainless steel shim stock, cut from 6 x 50-inch rolls\* using a single-edge razor blade and the template provided with the instrument. The liners were cleaned with organic solvent and then washed twice in boiling distilled water. After the second washing, the excess water was removed by centrifuging. The clean liners were stored in a carefully cleaned and sealed mason jar.

The mass distribution collection surfaces were placed in the collection cone using tweezers. They were touched only at the corners, and then only with washed rubber fingerguards. After sampling, the collection surface was removed from the cone, folded in half with the sample to the center, and creased, using tweezers. It was then taped at the unused corners to a clean piece of glass. Arcs of appropriate radii were scribed (similar to that shown in Fig. A-3) using dividers. The liner was then untaped and picked up with tweezers. While being held with tweezers, it was cut along the marked arcs with clean shears. The narrow, unexposed strips at the top and bottom of the surface were cut off and discarded. The folded sample strips were placed in a clean mason jar with a tight rubber-sealed lid.

The sample liners were cut into four strips. Except for the uppermost cut on the collection surface, the radii of the arcs would be chosen somewhat arbitrarily. Irregular deposition near the A.S. entry ports restricted the first cut to a radius of 9 cm or greater. Two considerations entered into the choice of radii for the other cuts: (1) Each strip had to be large enough to contain sufficient sample for analysis,

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\* Blaisdell Mfg. Co., 1342 Coronado Ave., Long Beach, California.

and (2) the cuts had to be made so that the values of deposition diameter  $D_G$  corresponding to them were fairly evenly spaced. In this program cuts were usually made at the following radii: 7.4 cm (top of the deposit), 9, 10, 11.25, and 14.4 cm (end of deposit). Blanks were determined from unexposed foils which were installed in the A.S., removed without sampling, and treated in the same way as the samples were treated. These techniques of preparation, handling, and analysis produced backgrounds of about 0.1  $\mu\text{g}$  S and 0.3  $\mu\text{g}$  Cl per strip.

The glass fiber sampling filters were washed twice in hot water distilled from an alkaline permanganate solution. The filters were supported between the layers of a folded piece of nickel screen during washing. The filters were then centrifuged and dried, still in the screen. They were stored in small sealed plastic bags until used. Batches of about 10 filters at a time were washed in this way. Backgrounds for each batch were determined from unexposed filters from that batch. These backgrounds were of the order of 1  $\mu\text{g}$  for sulfur and about 1.7  $\mu\text{g}$  for chloride.

#### B. Royco Particle Counter

The majority of the particle number size distributions presented in this report were obtained with a Royco Particle Counter, Model PC200 A.\* This instrument consists of three major systems: (1) the airflow system, (2) the optical system, and (3) the electronic system. A block diagram of the counter is shown in Fig. A-5.

A schematic representation of the airflow system is given in Fig. A-6. A small constant speed vane-type pump sucks air into the system through a tube of approximately 2 mm inside diameter at a flow rate of 300 cc/min. In this program it was unnecessary to use the dilution system because of the generally low particle concentrations.

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\* Royco Instruments, Inc., Menlo Park, California.

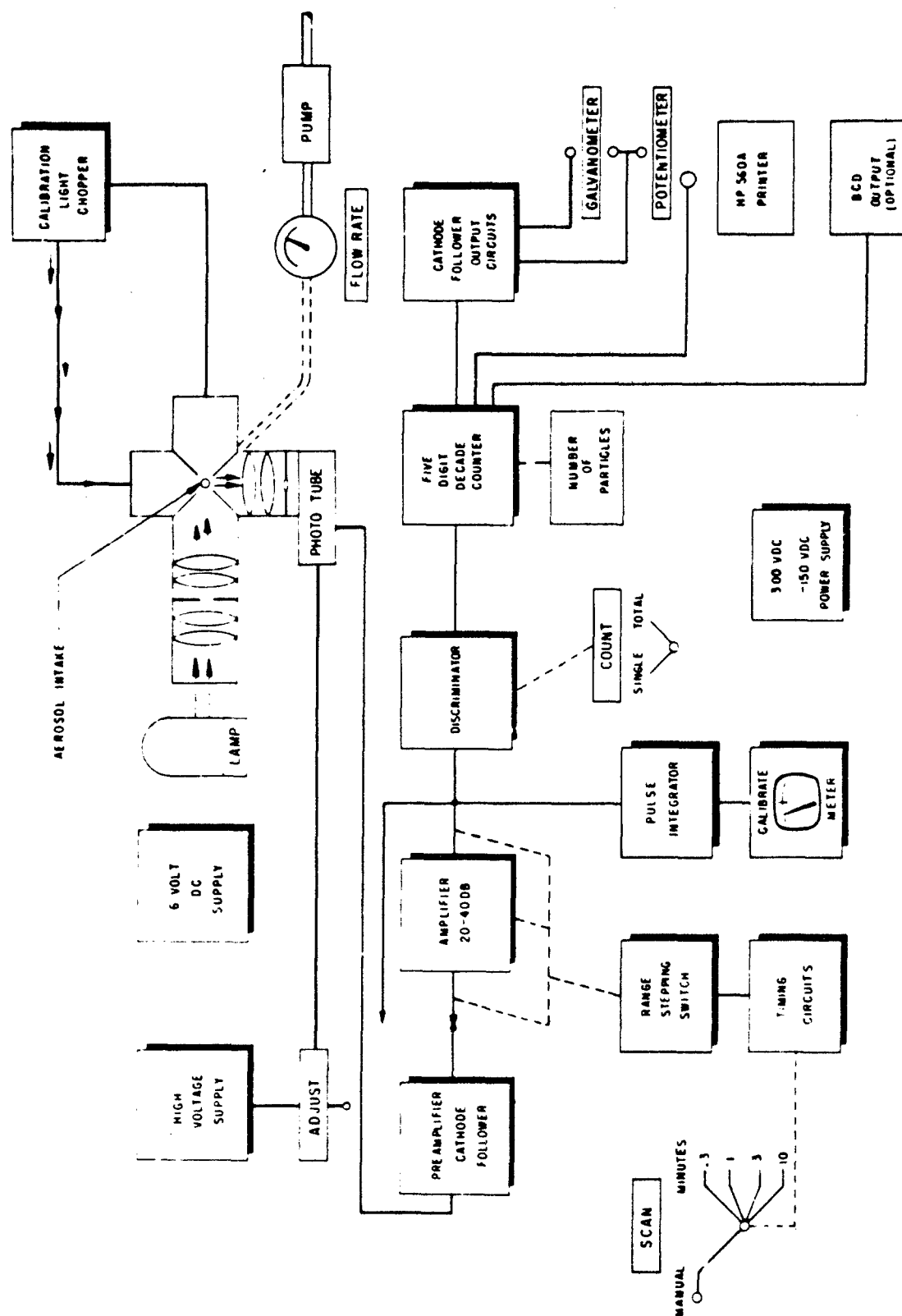
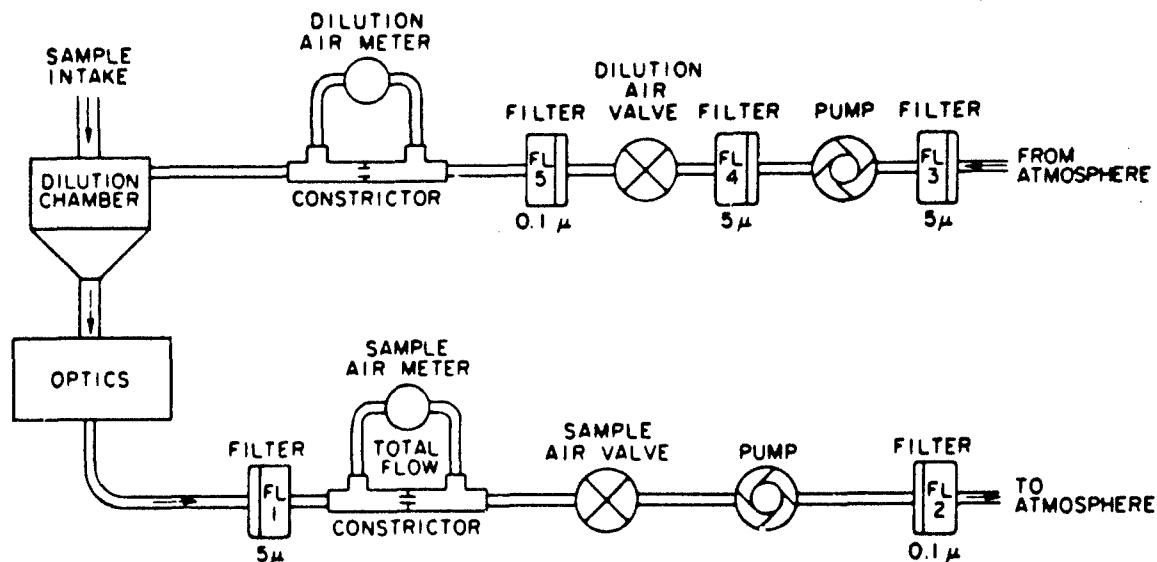


FIG. A-5 BLOCK DIAGRAM OF ROYCO PC200A PARTICLE COUNTER



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FIG. A-6 ROYCO COUNTER AIRFLOW SYSTEM

The optical system is shown in Fig. A-7. The axes of light projection, light collection, and air flow are mutually perpendicular. The chopper shown in the figure is used to generate a signal for field calibration purposes.

The electronic system consists of those parts shown in Fig. A-5. Of most importance are the photomultiplier which delivers a signal proportional to the light scattered by the particles in the sample volume, the discriminator circuits which classify the photomultiplier signals according to amplitude, and the counters which count the signals within certain amplitude ranges. The instrument can be operated so that only signals which fall within a specified amplitude range are counted, or all those greater than a certain amplitude are counted. Thus, the instrument can be used for counts within certain size ranges or for cumulative

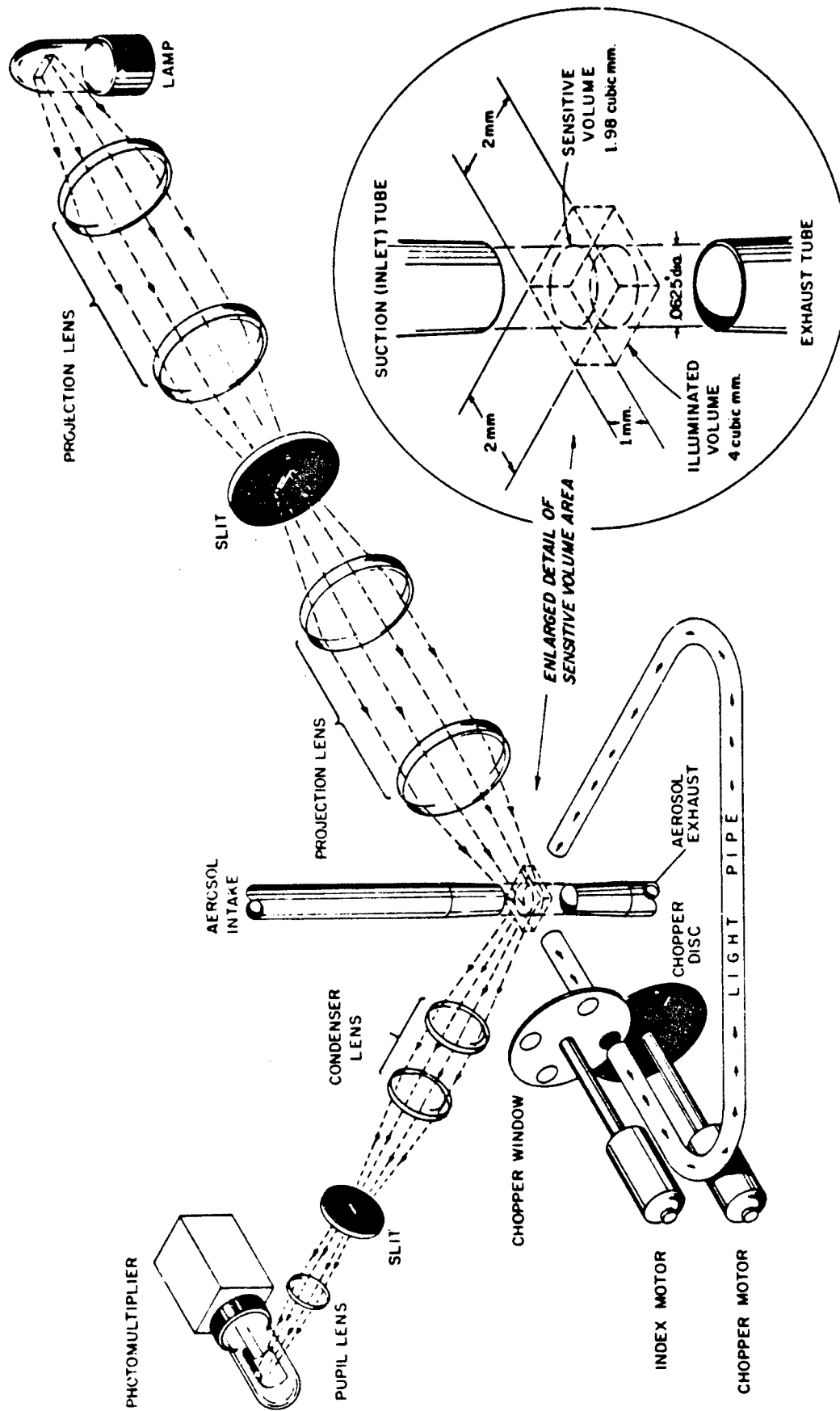


FIG. A-7 ROYCO COUNTER OPTICAL SYSTEM

counts. Only one channel can be counted at a time with this particular model of the instrument. Counting intervals available range from 0.3 to 10 minutes. The counts are recorded digitally on paper tape and are visually displayed on the front of the instrument.

The accuracy of the instrument depends upon, among other things, the reliability with which the amplitude of the 90-degree scattered light can be related to particle diameter. Amplitude of the 90-degree scattered light is not unambiguously related to particle diameter; there are refractive index effects also. The problems associated with this type of counter have been discussed by Hodgkinson and Greenfield (1965). The instrument used for this program was calibrated by the manufacturer using monodisperse polystyrene latex spheres. The size distributions sampled with the instrument are equivalent in their optical behavior to the stated size distribution of latex spheres. The radius intervals of the available channels of the Royco are given in Table A-I.

Table A-I  
CHANNEL CALIBRATIONS FOR ROYCO PHOTOMETER

Channel No.	Radius Interval, $\mu$	Channel No.	Radius Interval, $\mu$	Channel No.	Radius Interval, $\mu$
1	0.16-0.20	6	0.50-0.65	11	1.60-2.00
2	0.20-0.25	7	0.65-0.80	12	2.00-2.50
3	0.25-0.32	8	0.80-1.00	13	2.50-3.20
4	0.32-0.40	9	1.00-1.25	14	3.20-4.00
5	0.40-0.50	10	0.25-1.60	15	>4.00

The Royco was operated on the single channel mode rather than the cumulative. The numbers of particles in a given size interval and volume were averaged over several counting periods and then converted to the  $dN/d \log r$  form presented in this report.

### C. Condensation Nuclei Counters

Two different condensation nuclei counters were available for use on the program. The first of these, a General Electric small particle detector, Type CN,<sup>\*</sup> was used throughout the program. An improved version of the Scholz counter was available for use only on the second half of the program.

The General Electric counter is of the photoelectric type. The attenuation of a light beam is measured when condensation is caused to occur on the nuclei by expansion of the sample into a vacuum, and by the consequent adiabatic cooling. The calibration of this instrument is based on the work of Nolan and Pollak (1946).

While the General Electric counter is a relative instrument, measuring the attenuation of a light beam, the Scholz counter is an absolute instrument wherein the numbers of droplets formed in a volume during expansion are actually counted. The absolute counter should be more accurate than the General Electric counter, which depends for its calibration work with both absolute and relative counters by Nolan and Pollak. The chief drawback to the Scholz counter is that it takes substantial time to get a complete count and is somewhat tedious to use.

Generally, the data from the General Electric counter represented the average of the readings from five separate samplings and expansions. The Scholz counter was adjusted so that the dilution was such as to give, on the average, a few droplets per counting square. Then ten separate counts were made and averaged to give the data used. During the field program, numerous comparisons were made between the two instruments. The results of these comparisons are plotted in Fig. A-8. The scatter of the data is considerable. It may be due to statistical uncertainties or due to actual fluctuations in condensation nuclei because measurements with the two instruments were not made simultaneously. The more numerous G.E. counts were converted to equivalent Scholz counts using the curve

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<sup>\*</sup> General Electric Company, Schenectady, New York.

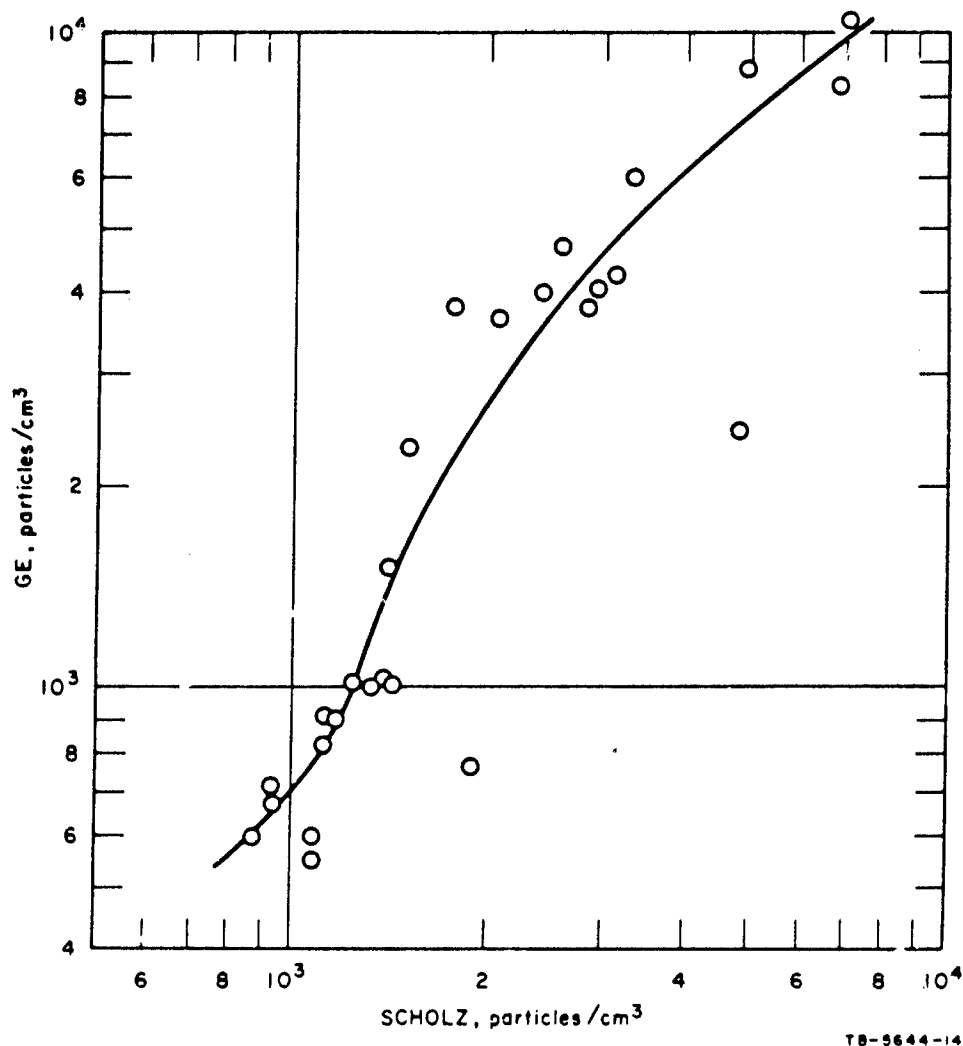


FIG. A-8 COMPARISON BETWEEN GE AND SCHOLZ COUNTERS

shown in Fig. A-8. These converted data were used for the calculations presented in this report.

#### D. Setup of the Equipment

The equipment was installed in a trailer on which three sides could be opened to allow free access of the instrument inlets to the ambient atmosphere. The trailer is shown in Fig. A-9 with the equipment in operation at Crater Lake during the second sampling period at that location.

During the first sampling period the instruments sampled directly from the air. During the second sampling period an inlet manifold was



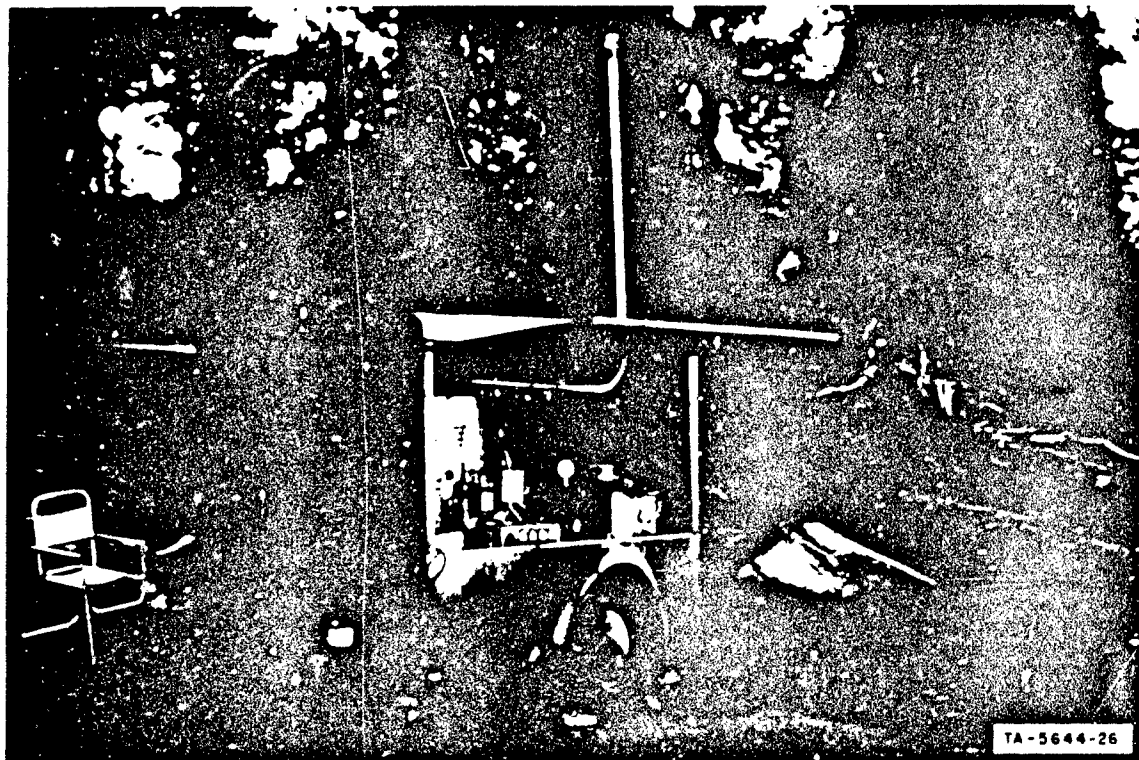


FIG. A-9 AIR SAMPLING TRAILER SET UP

used to bring the sampled air to the instruments from approximately 4 meters above the surface. This was done to minimize the effect of the low level dust which had been occasionally encountered during the first sampling period at Crater Lake. The manifold was made of 1-3/8-inch-diameter aluminum tubing with short (about 0.3 to 0.6 meters) lengths of 3/8-inch I.D. copper tubing connecting it to the instrument inlets. The manifold supplied air to all the instruments except two gas samplers and their preceding filters, used in an attempt to determine  $\text{SO}_2$  and  $\text{H}_2\text{S}$  concentrations. The inlet to the manifold was protected from rain by a shield which allowed air to enter freely from the sides, but not straight down the tubing.

In addition to the air drawn through by the samplers, approximately 20 liters/min of additional air flow was provided by a small pump connected to the end of the manifold. This minimized wall and settling losses.

At Crater Lake and Patrick Point, power for the equipment was provided by a gasoline-powered generator. The generator was kept well downwind of the instruments to prevent contamination from its exhaust. At Cape Blanco, power was available through the courtesy of the U.S. Coast Guard. The sampling location at Cape Blanco was upwind of the activity at the Coast Guard Station.

#### E. Weather Observations

Conventional surface weather observations were made at intervals of about an hour during the tests. The observers estimated sky cover and visibility and noted current weather. Temperature and humidity were determined with a small battery-operated psychrometer. Wind speeds were measured with a hand-held three-cup anemometer. The wind direction was estimated.

Appendix B  
ANALYTICAL METHODS

## Appendix B

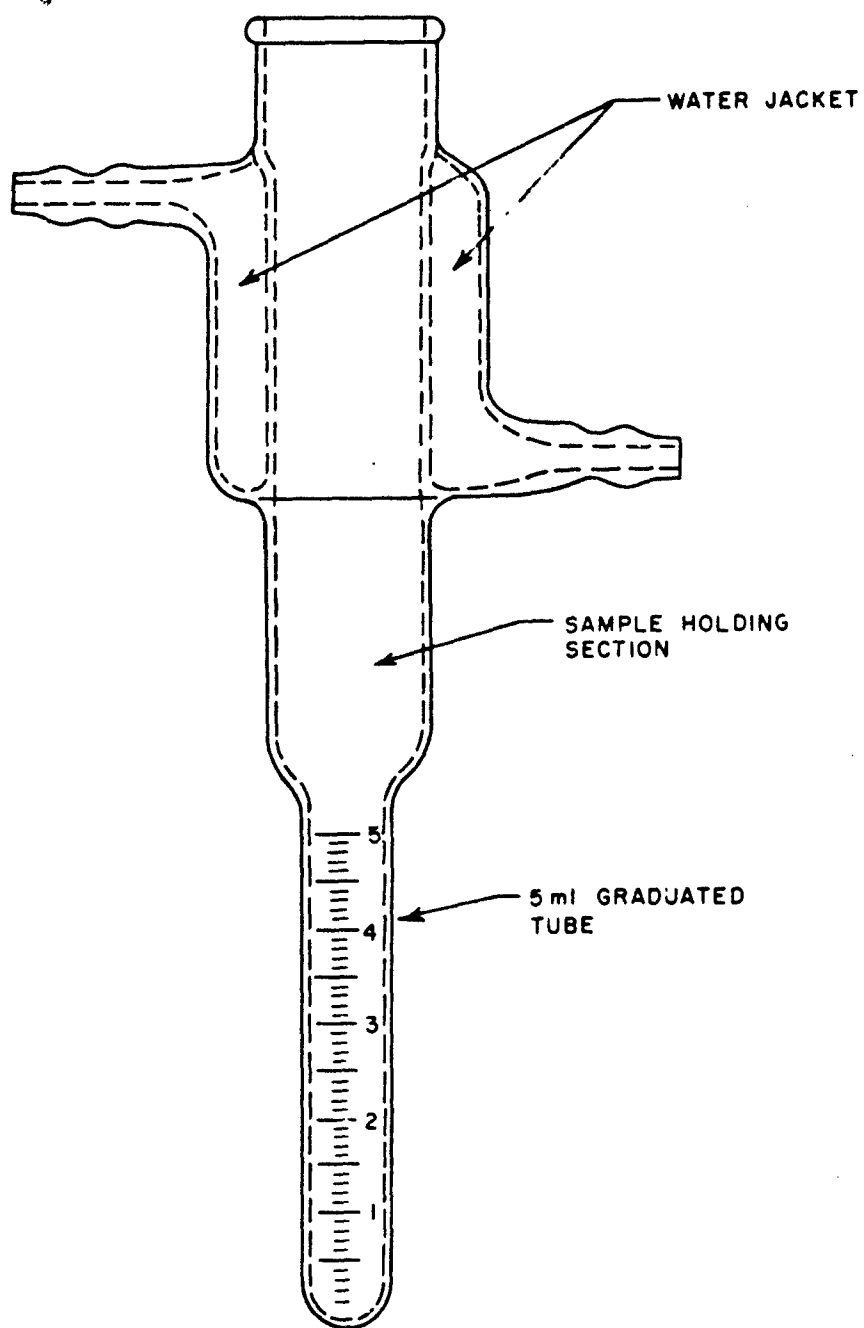
### ANALYTICAL METHODS

The analytical methods used in this program were originally developed for use in size distribution studies of urban aerosols (Ludwig et al., 1966). The method for sulphur determination makes use of a coulometric titration apparatus which is much like that originally developed by Coulson and Cavanagh (1960) for determination of chloride. In the procedure used on this program the sulfate is reduced to hydrogen sulfide in a microcombustion furnace. The hydrogen sulfide is determined by iodimetric microcoulometric titration using a modification of the chloride titration apparatus. Chloride amounts are determined by titration with coulometrically generated silver ions.

#### A. Extraction of Samples

The samples were extracted from the filters or the stainless steel strips by an apparatus specially designed for the purpose. This device, shown in Fig. B-1, has a 5-ml graduated pyrex tube at the bottom; above it is an enlarged section of approximately 17 mm I.D. and 5 cm long to hold the sample filter or A.S. strip. The section above the sample is a condenser of the same inside dimensions.

Analysis is begun by placing the filter or strip in the extraction apparatus. Exactly 4 cc of special water, described in greater detail below, is placed in the apparatus, cooling water is passed through the condenser, and the tube is heated carefully with a Meeker burner. During this operation the apparatus is clamped at a 45 degree angle to avoid bumping. The water is refluxed for 5 minutes. Then the filter strip is removed with clean forceps, and the cooling water is drained from the condenser. Heating is continued until only 1 to 2 ml of water remains in the apparatus. The apparatus is then cooled to room temperature. This extract serves as a source of aliquots for both the sulfur and chloride analyses.



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FIG. B-1 SAMPLE EXTRACTION APPARATUS

Since the procedure for the determination of sulfates or chlorides in particulate material collected on fiber-glass filters or on stainless steel discs or strips involves extraction with boiling water, the limit of sensitivity of the method is determined largely by the level of background material in the water used, and by the cleanliness of the extraction and sample collection apparatus. The major cause of high background, especially with chlorides, is due to residual material in the distilled water.

Water distilled from alkaline permanganate solution is usually satisfactory, but for the study of very low sample levels it is necessary to remove the last trace of chloride or sulfate. It was found that water distilled from an alkaline permanganate solution could be improved by passing it through a mixed bed, research grade, ion exchanger column. In the first trials, water was allowed to syphon from a 5-gallon bottle through an ion exchanger at the rate of approximately 2 gallons per hour. The ion exchanger was 10 inches long and approximately 3/4 inch I.D. and it was packed with Diamond Alkali ion exchanger ARM-381. This reduced the chloride (which was of primary concern) to approximately 0.1 ppm. Some further but slight improvement was observed if the water was passed through the ion exchanger several times. This slight improvement suggested that, if the small amount of water actually needed for analysis could be recycled through a resin bed a very large number of times, some gradual additional improvement should be expected. This proved to be the case, and with a small, rapidly circulating system it is now possible to prepare water with no more than 0.02 ppm of chloride as determined by silver coulometry. This level of chloride in the water represents no more than 0.08 microgram of chloride background per analysis in the actual procedure. By using water of this quality to pre-rinse the extraction apparatus, it is possible to keep the background chloride for the total analytical procedure down to less than 0.1  $\mu$ g. This does not include the residual amounts left in the filters and on the A.S. strips after cleaning.

The water purification, while primarily directed toward the removal of chloride; is also successful for the removal of the smaller traces

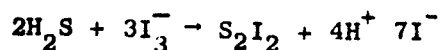
of sulfur-containing materials from the water. Sulfur was easier to remove than chloride. Remaining sulfur backgrounds are comparable to the chlorides.

#### B. Sulfur Microanalysis

After extraction, a measured aliquot of approximately 0.5 ml of the sample extract is placed in a small platinum boat along with five microliters of 0.5% sodium bicarbonate solution. To minimize the possibility of sample contamination from laboratory air, the water is evaporated from this sample by placing the platinum boat in a heated Pyrex tube with clean nitrogen flowing over the sample.

The boat with the sulfate-containing residue is then placed in the hydrogenation apparatus where the sulfate is reduced to hydrogen sulfide. The hydrogenation apparatus consists of a 900°C microcombustion furnace and a half-inch O.D. quartz tube which extends several inches beyond the hot zone on the inlet side and is fitted with a ball joint for coupling to a microcoulometric titration cell on the outlet side. The inlet side is fitted with a means for introducing the sample into the hot zone several minutes after the boat is placed in the cool section of the quartz tube and the tube closed. A 50-50 mixture of nitrogen and hydrogen is passed through the hydrogenation apparatus continuously at a flow rate of approximately 100 cc/min except when the system is opened for introduction of samples.

The titration cell is fitted with platinum generator electrodes, a platinum sensor electrode, and an iodine reference electrode. The reference electrode is filled with solid iodine in contact with a platinum wire and an electrolyte solution that is similar to that used in the titration compartment. An aqueous buffer solution containing 0.01% acetate acid, 0.2% sodium acetate, and 0.4% potassium iodide was used as the electrolyte. With this solution the titration reaction proceeds according to the following equation, giving three equivalents per mole of hydrogen sulfide.



The generator current is recorded, and the area under the curve is measured with a planimeter. The amount of  $H_2S$  and thus the amount of sulfur in the sample is determined from this area.

The electrolyte used has satisfactory efficiency for the absorption of  $H_2S$  without serious losses of iodine by volatilization. In general, it was necessary to make several determinations on standard samples, after the addition of fresh electrolyte, before recoveries became constant and quantitative.

On an operational basis there seems to be a narrow temperature range over which the titration proceeds satisfactorily. At lower temperatures, recoveries are low, at higher temperatures the baseline becomes irregular making it difficult to measure the area under the current-time curve accurately. For this reason, the titration cell was operated in a thermostated water bath of  $25 \pm 0.5^\circ C$ . Titrations have been successfully performed, using this arrangement, with ambient temperatures as low as  $15^\circ C$  and as high as  $32^\circ C$ . Thermostating the titration cell stabilizes the baseline by eliminating fluctuations in the rate of loss of iodine by volatilization and also by stabilizing the potential of the  $I^-/I_3^-$  reference electrode.

There is some uncertainty concerning the types of substances detected by this extraction--hydrogen reduction--coulometric titration procedure. Under ideal conditions sulfate can be quantitatively determined by this method. However, we suspect that some other sulfur-containing materials may also be detected. It is presumed that volatile organic substances containing sulfur would be steam-distilled out of the sample during the extraction procedure described above and hydrogen sulfide and sulfurous acid might also be boiled out of the extract. It is also possible that sulfites may be converted to sulfate in the sample preparation and that results obtained by this method may include part or all of the sulfite present in the sample.

### C. Chloride Microanalysis

A measured aliquot of the sample extract is pipetted directly into the chloride titration cell described by Coulson and Cavanagh (1960).



In the cell, the chloride ions are titrated by coulometrically generated silver ions in 70% acetic acid and 30% water. As in the sulfur titrations, the current is recorded and the area under the current-time curve is measured with a planimeter. The amount of chloride is calculated from Faraday's law of electrolysis:

$$\text{Equivalents of Chloride} = \frac{Q}{(96,500 \text{ coulombs/equivalent})}$$

where Q is the area under the curve in ampere-seconds.

The coulometer is highly damped to avoid overtitration. The bias setting is 230 mv vs. an Ag/AgOAc electrode. A current-limiting resistor of 0.22 megohm has been placed in the generator cathode circuit in order to keep a 10-mv recorder on scale on the 128  $\Omega$  setting.

The very slight solubility of the halides,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , makes the method quantitative for these ions to less than 0.01 microgram. This amount may be contained in as much as 0.5 ml of water. Blank corrections for residual chloride in the distilled water were usually necessary, but are quite small with the specially prepared water which has been discussed earlier.

The coulometric titration, as carried out in these studies, does not distinguish  $\text{Cl}^-$  from  $\text{Br}^-$  or  $\text{I}^-$ , but the ratios of bromide to chloride and of iodide to chloride are quite small (generally less than 0.05) in unpolluted atmospheres (e.g. Duce, et al., 1965). Thus it is probably reasonable to assume the analyzed material to be chloride.

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